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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

EDWARD L. NICHOLS

ERNEST MERRITT, and FREDERICK BEDELL

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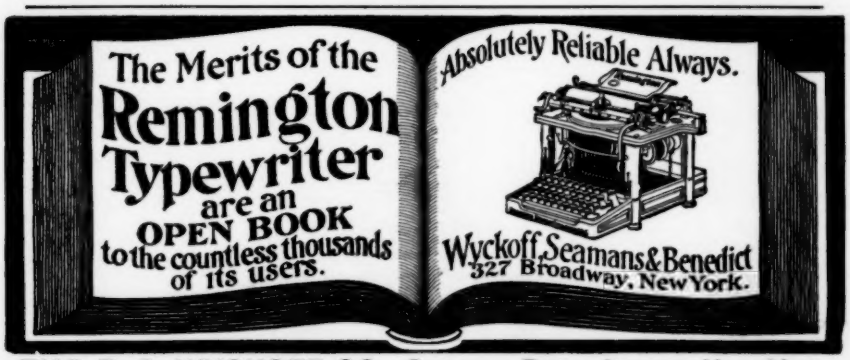

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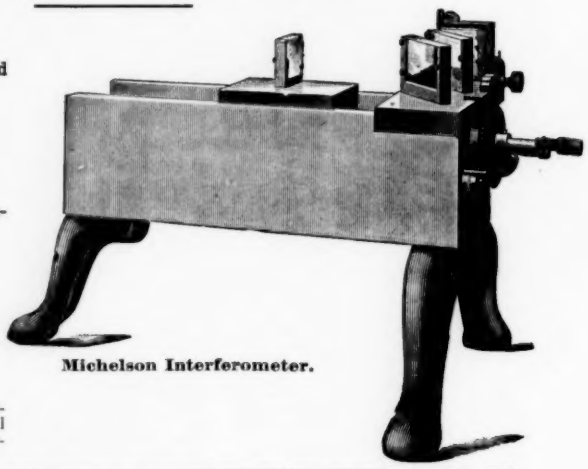

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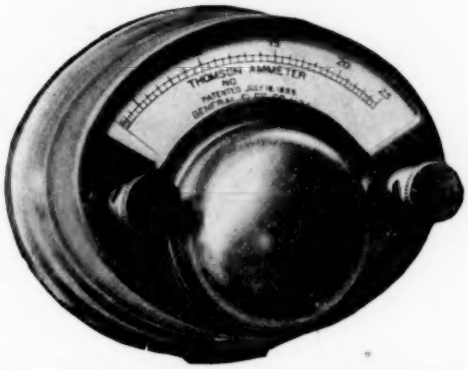

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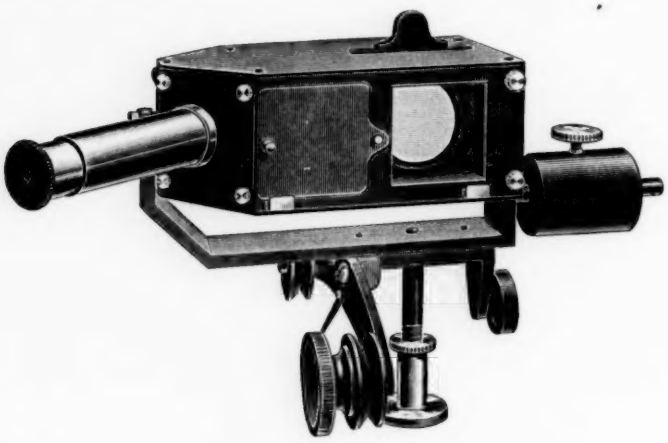

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PHYSICAL REVIEW.

FALSE SPECTRA FROM THE ROWLAND CONCAVE GRATING.

By Theodore Lyman.

IT is proposed to show in the following paper that among the spectra formed by the Rowland concave gratings there are spectra not accounted for by the ordinary theory of the grating; that such spectra are common and at times fairly strong and of excellent definition; that these spectra are diffraction spectra, of much less dispersion than the ordinarily recognized spectra, and that the errors of ruling to which they are due are not local but general to the whole surface of the grating. Finally it is proposed to explain an experimental method by which these false lines can be sorted out from the regular and calculable overlapping spectra. These lines are especially dangerous in series spectra work, giving a somewhat systematic reproduction of strong lines and groups, which reproductions in actual vibration frequencies do not exist. There is probability and some evidence that such errors have been committed in the past, and it was in the presence of this danger that the false spectra were here discovered.

In the year 1893, Schumann showed that the ultra-violet spectrum could be extended to the neighborhood of 1,000 μ. He used a spectroscope fitted with a fluorite prism and fluorite lenses. The apparatus was so constructed that it could be enclosed in a case from which the air could be exhausted. According to his investigation, it was chiefly the absorption of the air for light of very short

wave lengths that had prevented other investigators from extending the spectrum below wave length 1,800 μ. Owing to the nature of a prism spectrum, it was difficult for Schumann to determine accurately the wave lengths of the lines which he discovered. Since his paper, no attempt seems to have been made to measure these lines. It was in an effort to determine these wave lengths that the false spectra above referred to were first observed.

It seemed probable that if a concave grating could be used to obtain the ultra-violet lines, an accurate determination of their wave length would be possible. Accordingly, some two years ago, Mr. E. H. Colpitts and the writer undertook the investigation. The methods used and the results obtained were briefly as follows:

The concave diffraction grating, slit and photographic plate were all enclosed in an air-tight cast iron box. Light was admitted to the box through a fluorite window. The source of light was a powerful electric spark, obtained from a transformer run from the commercial circuit; a capacity equivalent to four large Leyden jars was placed in parallel with the spark gap; magnesium was used for terminals. Following Schumann's work, the air was exhausted from the box. The spark was placed close to the fluorite window in order that the column of air between the source and the plate should be as short as possible. Under these circumstances a photograph was obtained showing lines apparently down to wave length 924 μ, a value lower than Schumann's lowest estimated wave length. Terminals of aluminum, cadmium, cobalt, nickel and copper were tried. All showed lines below 1,800 μ; some showed lines as far down as position 950 μ.

During these experiments, the air pressure in the apparatus did not always have the same value. Some plates were taken with the pressure as high as 1 cm.; others with it as low as .2 cm. It was observed that this difference in pressure did not have any effect on the strength of the lines. Up to this time the first spectrum had been used; now it was desired to find these lines in the second spectrum. In spite of the greatest care, however, no trace of any line below 1,900 μ could be found in the second spectrum.

The absence of the lines in the second spectrum, together with their behavior under small differences of air pressure, raised the

suspicion that, either the lines were not due to light of a very small wave length, or that light of very short wave length was not absorbed by the air to the extent indicated by Schumann. To test this idea the spark was first removed to a metre's distance from the fluorite window. This air column did not reduce the intensity of the new lines. Next air was admitted to the box, and still the lines were unchanged in intensity, even through a column of air now five metres long. Evidently the lines were not absorbed by air.

Lest the special brand of plate employed was particularly sensitive to the extreme ultra-violet, a number of different plates were tried. In each case a good photograph was obtained showing practically all the lines.

A piece of window glass was placed between the slit and spark and no trace of the lines could then be found. Since the light causing these lines is absorbed by glass and is not absorbed by air, it would seem to have a wave length between 3,500 μ and 2,000 μ, according to the accepted absorbing power of these two media.

It was now observed that the groups in the magnesium spectrum at 2,790 μ, 1,873 μ and 924 μ were, even to casual inspection, strikingly characteristic and identical in general appearance. Further, on measuring their dispersions, they were found to be proportional to the displacements of the groups from the slits. Therefore, these groups formed either a remarkable series reproduction or a heretofore unobserved diffraction phenomenon. Thus the issue was definitely raised whether these lines were real first spectrum lines, produced by light of wave lengths 924, 1,873 and 2,790, and arranged in a 1, 2, 3 series, or whether they were all produced by light of one wave length and owed their position to some diffraction phenomenon connected with the grating.

To distinguish between these alternatives, recourse was had to the relative refrangibility of these lines through quartz. To this end a small angle quartz prism was placed between slit and grating and a short distance from the slit. The effect of this prism was to produce virtual images of the slit whose displacements were nearly proportional to the refrangibility of the light. This device resulted in the displacement of each line in the grating spectra by an amount proportional to the refrangibility of the light producing that line.

If the lines at 1,873 μ and 924 μ were caused by light of the same wave length, they would suffer equal displacements. If they were caused by light of different wave lengths, they would be displaced by different amounts.

The experiment was tried and it was found that the groups at 2,790 μ, 1,873 μ and 924 μ all suffered about equal displacements. From 2,790 μ down to the region of 1,873 μ, the displacement of the groups increased as the wave length decreased. There was then a discontinuity in the rate of increase of the displacement before 1,873 μ and a second discontinuity between 1,873 μ and 925 μ.

The most obvious conclusion from these data is that the lines at 1,873 μ and 924 μ are not due to light of wave lengths corresponding to the positions of the lines in the spectrum. They seem to be caused by light having a wave length near 2,800 μ; they seem to be reproductions of some part of the true spectrum, curious phantom lines due to some property or imperfection of the grating. An examination of the lines below 1,900 μ taken with aluminum terminals fully carried out this theory.

Before leaving this first grating, which we will call No. 1, it is important to note that although the groups in magnesium at 2,790 μ, 1,873 μ and 924 μ closely resemble each other, their wave lengths are not exactly in the 1 : 2 : 3 ratio, $2 \times 924 = 1{,}848$ which differs from 1,873 by 25 μ.

It was proved that these phantom lines were not due to any local variation in ruling by shielding all but a narrow strip of grating surface, and then moving the screen so as to expose each strip in turn. In this way a series of photographs were obtained, each from a different strip of grating surface. They all showed the phantom lines with about equal intensity.

In addition to the grating with which the investigation was begun, three others were examined. Two of these were of larger radius—21 feet, the other was similar in type to the first instrument. Of the two large gratings, one showed the phantom lines distinctly. The two strong groups formerly at 1,873 μ and 924 μ were now found at positions corresponding to 1,728 μ and 1,079 μ. The other large grating did not show the lines at all. The last small grating showed the reproduction of group 2,790 μ at positions of about

1,870 μ and 924 μ. In addition, however, there were also numerous less distinct reproductions scattered between these two positions.

We may now sum up the facts arrived at in these few pages. Of four concave diffraction gratings examined in this investigation, three showed the phenomenon of phantom lines. These lines vary in position with the grating by which they are produced, but the variation cannot be connected either with the variation of radius of curvature of the grating or with the number of lines to the inch. The most prominent of these phantom lines closely resemble some group in the true spectrum. This repetition of a true group occurs most strongly twice. The width of these phantom repetitions is proportional to their apparent wave length. The wave lengths of the true group and its phantom repetitions bear no simple relation to one another. The photographs obtained with gratings 1 and 4 show a very large number of faint repetitions of a group or set of groups. These repetitions form a sort of background to the main spectrum between 1,800 μ and 900 μ.

A more detailed account of the apparatus and of the numerical results of the investigation will now be given. The consideration of the causes which produce these phantom lines is left for the end of the paper.

Fig. 1.

The first grating investigated was one of 180 cm. radius. The plate was prepared by Brashear and ruled by Rowland's engine in the year 1897; it had 14,438 lines to the inch. To economize space a mounting somewhat different from that of Rowland was used. The grating and slit were fixed in position at a distance apart equal to the radius of curvature of the grating. The plate-holder was carried by an arm pivoted at a point on the line connecting slit and grating and midway between the two. The length of the arm was, of course, half the radius of the grating. The plane of the grating was so adjusted that the principal image fell about 2 cm. to the right of the slit. This was done to avoid reflection from the polished jaws of the slit. The plate-holder was constructed to take a plate 5 inches long and 1 inch broad. The form of the box in which the apparatus

was enclosed is not material to this investigation. The spark which served as a source of light was placed within 3 mm. of the fluorite window. In the first experiments the width of the slit was about .1 mm. and the time of exposure was about 1 hour. Later, however, good photographs were obtained with exposures of from 12 to 15 minutes. In making tests for the absorption of the air a quartz lens was placed between the source and the slit.

In developing photographs of this type, great contrast is the chief object. The kind of developer used thus becomes important. After several trials, an Ortol-Soda developer was found to give the best results.

The apparent wave lengths of the different lines which come under consideration were determined by comparison with the normal sun spectrum. A dividing engine with a ½ mm. screw was used. This screw, when used to measure lines on a 6-foot grating possesses for a run of 20 cm. an accuracy better than one one-hundredth of an Ängström unit. The plate was observed by means of a stationary microscope fitted with a 4-inch objective and micrometer eye piece. The value of one centimeter of plate length in terms of Ängström units was determined by measurements taken between two given sun lines, located by Rowland's map. In order to get a photograph of the sun spectrum and the magnesium spectrum on the same plate, a shutter was placed before the slit and so adjusted that the upper or lower half could be exposed at pleasure. By this means two narrow spectra were obtained, one above the other. The method is preferable, when working with the first spectrum, to the usual mode of protecting the plate itself by a swinging screen.

When it became necessary to test the nature of the light producing the lines at 1,873 μ and 924 μ in the magnesium spectrum, the following arrangement was adopted. The quartz prism of an angle of 5 degrees was placed some 30 cm. distant from the slit, but not on the straight line joining slit and grating. Thus when the source was in position A, the light did not fall upon the prism; but when it was in position B, the light passed through the prism. In the first case, the upper half of the slit was closed by the shutter; in the second, the lower half was closed. The result was, of course, to produce two spectra, one above the other; the one due to light

(To face page 7.)

Fig. 3.

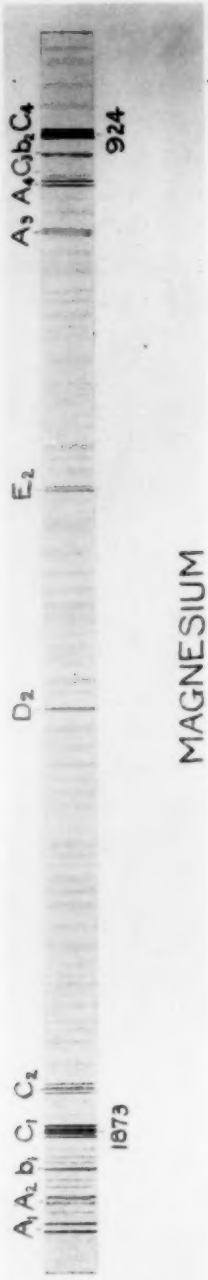

Fig. 4.

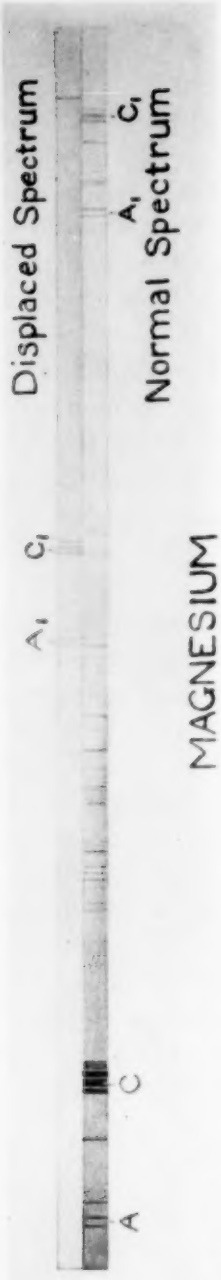

Fig. 5.

LYMAN: FALSE SPECTRA FROM THE ROWLAND CONCAVE GRATING.

which had passed through the prism was thus shifted toward the red. The general appearance may be seen from Fig. 3, Plate 1.

It now becomes necessary to consider more in detail the behavior of the light of these ultra-violet spectra when passed through the quartz prism. The results for magnesium may be seen from the following table. The lettering of the groups on the plans of the spectra is, of course, arbitrary. The chief or real groups are marked with an unsubscripted letter. The reproductions are marked with letters bearing a subscript. The plates are from drawings made from the original photographs. Beginning with magnesium, Fig. 4, six principal groups of lines are to be noted, they extend from the pair of lines marked A_1, wave length 1,966 μ to the strong group C_4, wave length 924 μ. Besides these strong lines, there are six fainter groups distinctly visible, A_2, B_1, C_2, A_3, B_2 and C_3. A_2 resembles group A_1, C_2 group C_1; C_3 resembles group C_4, A_3 group A_4. It is to be noted that while A_2 and C_2 lie on the right or ultra-violet side of A_1 and C_1, C_3 and A_3 lie on the left or red side of C_4 and A_4. In addition to the simple groups of lines already mentioned, the whole spectrum, from one end to the other between A_1 and C_4 is filled with a number of fine, faint lines. These lines are not regularly arranged so as to produce fluting, but rather present the appearance of a reproduction of groups of lines.

Fig. 2.

If we examine the displacements produced in these groups when the light is allowed to pass through the quartz prism before falling upon the grating, the following facts become evident. A steady increase in displacement is observed in the successive lines going from the strong group at 2,790 μ (C) towards the ultra-violet until we get in the neighborhood of group A_1. At this point the amount of displacement suddenly returns to about the value it had at 2,790 μ. Between groups A_1 and D_2 the displacement suffers a second discontinuity. Thus A_1 gives 42.1 mm., D_2 39.8 mm. The displacement of C_4 is almost exactly that of C_1 and very nearly that of group C, 2,790 μ. The figures are 42.25 mm., 42.25 mm., 42.21 mm. As stated before the most obvious conclusion from these data is that the lines A_1 to C_4 are not due to light of wave lengths corre-

sponding to the positions of the lines in the spectrum. They seem to be reproductions of some part of the true spectrum.

On the aluminum plate, there are present six strong lines B_1, C_1, D_2, E_2, B_3, C_3 with wave lengths from 2075 μ to 933 μ. There are faint reproductions of these groups similar in arrangement to those observed with magnesium. There is a background of fine indistinct lines. On allowing the groups to be displaced by the prism, we find group D_2 less displaced than group C_1, and group B_1 less displaced than a real group called *I*.

Magnesium.

Group.	Apparent wave length.	Displacement.
C.	2790 μ	42.2 mm.
I.	2713.	43.4
II.	2682.	43.9
A_1.	1966.	42.1
A_2.	1924.	
b_1.	1914.	
C_1.	1873.	42.2
C_2.	1834	42.3
D_2.	1475	39.8
E_2.	1266	40.2
A_4.	969	41.9
C_3.	964	
b_2.	944	
C_4.	924.	42.2

Aluminum.

Group.	Apparent wave length.	Displacement.
I.	2376 μ	38.8 mm.
B_1.	2075	36.1
C_1.	1890	36.7
D_2.	1300	34.9
E_2.	1184	35.3
B_3.	1023	36.0
C_3.	933	36.6

We may now consider the false nature of the lines as established. It remains to investigate the causes which produce this diffraction phenomenon.

It is perfectly evident that the phantoms are not due to a local variation in the rate of ruling, such as produce ghosts; for we have

seen that the fault is not local in the grating surface. Moreover, we know that a ghost always occurs close to the line of which it is a reproduction.

The phantoms are not due to a false source of light since the dispersion of the various reproductions is not the same as that of the real group. We may discard the hypothesis that the mounting of the grating or the position of the source of light has any effect. The lines occur with various forms of mounting and with various positions of lens and source, as will be seen later. We have to deal with a diffraction phenomenon, with an inherent property of the diffraction grating itself.

It seems probable that in developing the theory of the grating some assumptions have been made which are not according to fact. It is in the error of such assumptions that we must seek the solution of our problem.

It is generally assumed in treating the grating that the lines of the ruling are of equal width and are separated by equal spaces. In the very nature of things, it is evident that this cannot be the case in view of the very minute distances involved and the almost inconceivable rigidity of the ruling engine which would be necessary. These variations, slight in absolute amount, may be a considerable fraction of the distance from line to line. It is clear, moreover, on experimental as well as on the theoretical ground that these variations are not local but extend over the whole surface of the grating.

It appears, then, that the departure from equal spacing assumed in the theory of the concave grating, is not the random departure which is next in theoretical simplicity, but a more or less systematic departure which has emphasized disproportionately certain of the subordinate maxima called for in the conventional theory. If the position of the false maxima occurred in the ratio 1 : 2 : 3, or in any other simple ratio, the phenomena would invite an analytic discussion. As an experimental fact, however, our lines are not harmoniously placed with respect to the slit, nor are they arranged according to any discoverable system. Moreover, they are different in character and position when obtained by different gratings ruled by the same engine. It seems most likely that the phantom lines are due to a number of superposed first spectra of varying dispersions;

and that these false spectra owe their existence in some manner to the variation in width and separation of the grating lines. Under these conditions, an analytic discussion seems less profitable than the presentation of the experimental data.

In order to substantiate the statements just made, it becomes the next object of the investigation to observe carefully the relative positions of the phantom lines, not only in one, but in several different gratings.

We must carefully observe, in looking over the tables already given, that although several groups bear a strong resemblance to each other, and though the apparent wave length of these groups are nearly in one, two, three ratio, this ratio is never exact.

In aluminum, the line C_3 seems to resemble the line C_1, but $2 \times 933 = 1{,}866$ not 1,890. The group B_3 resembles B_1, but $2B_3 =$ 2,046, not 2,075. There certainly is no exact 1, 2, 3 relation, although lines corresponding roughly to $3C_3$ and $3B_3$ in wave length may be found for aluminum. The difference between 2,046 μ and 2,075 $\mu = 29$ Ångström units cannot possibly be due to the error of observation. It is perfectly safe to say that the measurements of wave lengths in the table are correct to 1 Ångström unit.

Before examining another grating, there are one or two more points which need attention. A concave grating produces two spectra of the first order, which in this form of mounting lie on each side of the slit. The spectrum on the left had been investigated, it was now necessary to observe the spectrum on the right of the slit. The grating was therefore turned upside down, by which process the spectrum formerly on the right of the slit now fell upon the left. Photographs taken showed the lines, A_1, C_1, A_4, C_4, etc., in magnesium as clearly as before. The grating was next turned about a vertical axis until the direct image of the slit fell upon the plate. No lines below group C_4 were revealed by this process, nor was the position of the lines greatly changed. It must be noted, however, that the turning of the grating will somewhat distort the spectra and change the value of μ to cm.

The second grating to be investigated was of 21 ft. radius, 14,438 lines to the inch. It was arranged on Rowland's mounting. The intensity of the spectra given by this grating was very inferior

to that obtained with the 6 ft. instrument. The first spectrum was selected to work with, the magnesium spark was used as a source. It was found necessary to give an exposure of an hour and to use a slit .2 mm. in width. A good deal of care was taken to have the exposure of the proper length; if too short, the lines themselves would not appear; if too long, the lines would be obscured by fog. With this 21 ft. grating, a very little fog would quite shield any very faint line. After some trouble, the characteristic reproductions of group 2,790 μ were found. They now occurred, however, at positions corresponding to wave lengths of 1,728 μ, 1,079 μ. The widths of the groups were 4.8 mm., 2.8 mm., 1.8 mm. Thus, though these phantom lines have different apparent wave lengths when measured on different gratings, their dispersion seemed proportional to the wave length. It must be noted that with grating No. 2 only the lines called A_1, C_1, and A_4, C_4 are visible; the other fainter lines, as well as the fluted effect in the background being totally absent. This is well accounted for by the feebleness of the spectrum obtained from grating No. 2. The apparent wave length of these groups was obtained by the same method as that previously employed. Owing to the great distance between the head group (2,790 μ) C and its reproductions, a cathetometer was used. The results are correct, however, to better than 2 Ängström units. The widths of the groups were measured on the dividing engine and are correct to within .03 mm. The value of 1 cm. of plate length was obtained from measurements between two sun lines.

It would be interesting to take groups C_4 and C_1 on one very long plate, and group C_4 and the image of the slit on another. By this method the wave lengths of C_4 and C_1 could be very accurately determined. As it is, however, I feel certain that groups 2,790 μ C_1 and C_4 as obtained with grating No. 2 are not in 1 : 2 : 3 ratio.

The next grating investigated was one of 21,000 lines to the inch and 21 ft. radius. Here the illumination was even more feeble than with grating No. 2. Great trouble was experienced from fog. The lines in magnesium, C_1 and C_4 could not be found. The last grating examined was similar to No. 1. It has a radius of 183 cm., 14,438 lines to the inch; it was prepared by Brashear; it was

ruled by Rowland's engine at Johns Hopkins in the year 1894. The mounting was the same as that of grating No. 1.

The character of the photographs obtained with grating No. 4 was quite different from those obtained with grating No. 1. Lines A_1, C_1 and A_4, C_4 were present and with about the same apparent wave length as before. They were, however, very much less distinct than when obtained with grating No. 1. The fluting effect was not very sharp; but, on the other hand, the space between positions 1878 μ and 924 μ was filled with reproduction of groups A_1 and C_1, of such clearness as to be quite unmistakable. The wave lengths of some of these phantom lines was determined in the same manner as before. Groups corresponding in appearance to the family marked A_1 A_2 A_3, etc, were found at 1,970 μ 1,020 μ and 993 μ and 970 μ. The group called C_1, C_2, etc., were found at 1,878 μ and 924 μ very clearly, and at more than eight other positions in a less distinct form between 1,878 μ and 924 μ. In fact, the spectrum in this region is so filled with groups of the A, C type that the lines of one family overlap lines of the other in many cases.

Such, then, are the experimental data connected with this phenomenon. Before coming to a statement of conclusions, however, the following facts are of interest.

Some of the reproductions belonging to the set of lines A_2 and E_2 in aluminum occur under the real spectrum and may be observed if proper care is used.

Gratings of large radius do not show the false lines with as much clearness as gratings of small radius. So feeble indeed are the false lines obtained with the 21 ft. grating that it is improbable that they would be noticeable in ordinary spectrum work. With a six foot grating, however, the false lines are so strong that they might easily cause errors in series spectrum investigations. We have seen, moreover, that the false lines from grating No. 1 are much stronger than those from grating No. 4, and we have reason to suspect that gratings exist which produce false lines even stronger in character than those obtained with grating No. 1. Gratings 1 and 4 differ little in radius and have exactly the same number of lines to the inch, yet their false spectra are entirely different in character.

We cannot apparently predict the nature of the false spectra of one grating from the false spectra produced by another of the same ruling and radius.

The conclusions arrived at in this paper may be stated as follows:

1. The first spectrum produced from the Rowland concave grating is not pure, but is complicated not only by underlying spectra of higher order, but by the presence of a number of spectra of lower dispersion than the chief spectrum.

2. The number and dispersion of these false spectra obey no simple law.

3. The number, dispersion and clearness of these spectra differ with different gratings.

4. The lines due to the false spectra are most clearly visible in the extreme ultra-violet, owing to the absence of strong real lines, and are so pronounced as to screen the feeble real line that may occur in this region.

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY,
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A MODIFICATION OF THE USUAL METHOD OF DETERMINING TRANSFERENCE NUMBERS AND AN INVESTIGATION OF THE INFLUENCE OF THE CONCENTRATION ON THEIR VALUES IN THE CASE OF SOME TRI-IONIC SALTS.

BY ARTHUR A. NOYES.

1. PURPOSE OF THE INVESTIGATION.

AS has been frequently pointed out, the dissociation of tri-ionic salts, such as potassium sulphate and barium nitrate, like that of most dibasic acids, might well be expected to take place in the two stages expressed by the following equations:

$$K_2SO_4 \rightleftarrows K^{\cdot} + KSO_4' \quad \text{and} \quad KSO_4' \rightleftarrows K^{\cdot} + SO_4'',$$
$$Ba(NO_3)_2 \rightleftarrows BaNO_3^{\cdot} + NO_3' \quad \text{and} \quad BaNO_3^{\cdot} \rightleftarrows Ba^{\cdot\cdot} + NO_3'.$$

Up to the present time, however, no conclusive experimental evidence of the existence of such intermediate complex ions as KSO_4' and $BaNO_3'$ has been presented. The freezing-point lowering and electrical conductivity of such salts prove, to be sure, that, even in moderately concentrated solutions, the intermediate ions, if they exist at all, are present only in relatively small amounts. Nevertheless, the question is still unanswered, whether the portion of the salt that is not completely dissociated consists wholly of undissociated molecules (K_2SO_4 and $Ba(NO_3)_2$) or mainly of the partially dissociated ones (KSO_4' and $BaNO_3^{\cdot}$). The answer to this question cannot be reached by the method used in the case of dibasic acids, since it is only for hydrogen and hydroxyl ions that we possess specific quantitative methods of determination. The property adapted to throw the most light on the matter would seem to be the change of the transference numbers of such salts with the concentration; for if KSO_4' or $BaNO_3^{\cdot}$ ions exist in moderately concentrated solution and if these ions are dissociated in diluter solu-

tions, as they must be, into $K^{\cdot}$ and SO_4'' or $Ba^{\cdot\cdot}$ and NO_3 ions, it is evident that the proportion of potassium or barium transferred in the differently concentrated solutions will be markedly different.

This investigation was therefore undertaken in order to determine the effect of dilution on the transference numbers of some tri-ionic salts. Since the results, to be of much value in connection with the theoretical question just referred to, must have a high degree of accuracy, my first efforts were, however, devoted to perfecting the usual method of determining transference numbers, and these have led to a modification of it, which it is one of the main purposes of this article to describe.

2. Results of Previous Investigators.

Before describing my own experiments, the results of previous investigators bearing directly on the subject may be mentioned.

In the first place, it may be recalled that various investigators have proved that the transference numbers of *di*-ionic salts do not vary with the concentration, provided the latter does not exceed a moderate value, for example, 0.5 mol per liter. Thus, this has been shown by Hittorf in the case of potassium chloride, bromide, iodide, chlorate, nitrate, cyanide, and acetate, ammonium chloride, sodium chloride, nitrate, and acetate, and silver nitrate. This constancy of the transference numbers has been confirmed by other investigators[1] in the case of many of these salts, and has been found by Loeb and Nernst[2] to apply also to silver acetate and silver ethylsulphate. The only exceptions thus far discovered are in the cases of lithium iodide and chloride, which have been found by Kuschel[3] and Bein[4] to behave like the halides of the alkaline-earth metals (see below). Aside from these exceptions, which are probably to be explained by assuming the formation of intermediate complex ions, the statement made above in regard to the non-variations of transference values with the dilution holds true.

[1] For the original literature on transference determinations, see Bein, Ztschr. physik. Chem., 27, 1. For a summary of all existing values for concentrations up to 0.1 normal, see Kohlrausch, Wied. Ann., 66, 816.

[2] Ztschr. physik. Chem., 2, 948.

[3] Wied. Ann., 13, 289.

[4] Ztschr. physik. Chem., 27, 50.

Hitherto only very few tri-ionic salts have been satisfactorily investigated in this direction. Aside from the earlier experiments of Hittorf, Weiske, Kuschel, and others, which are not sufficiently accurate to throw any light on the present question,[1] and aside from the more recent experiments on the halogen compounds of cadmium and zinc, which exhibit unusually complicated relations, the only determinations available for our purpose are those of Bein[2] on barium, strontium, and calcium chlorides, and of Hopfgartner[3] on barium chloride. It is desirable that even these determinations should be confirmed, since the results obtained are somewhat remarkable in their character. It was found, namely, that the transference number of the cathion increases with increasing dilution, which is just the opposite of the effect which would arise from the presence of $BaCl^{'}$ or $CaCl^{'}$ ions in the more concentrated solution. Barium chloride was, therefore, included among the salts which I have investigated. The significance of the behavior which it exhibits will be further considered below.

3. DESCRIPTION OF THE METHOD.

As is well known, the principal difficulty met with in determining the transference numbers of salts for which electrodes of the same metal can not be used arises from the fact that free alkali and acid are generated at the cathode and anode respectively and that the hydroxyl and hydrogen ions thus produced, on account of their high rates of migration, rapidly pass into the middle portions of the solution, thus changing its composition and its transference relations.[4] This change in composition can be greatly retarded on the anode side by the use of a cadmium electrode, since the cadmium ions that pass into solution have a rate of migration very much smaller than that of hydrogen ions. This kind of anode has in fact been generally employed.[5] There has been, however, no

[1] Compare Bein, Ztschr. physik. Chem., 28, 439–452, in regard to the errors of the early determinations; also Kohlrausch, Wied. Ann., 66, 818, in regard to the disagreement of the results of them.

[2] Ztschr. physik. Chem., 27, 50, 51.

[3] Ztschr. physik. Chem., 25, 137.

[4] See Bein, Ztschr. physik. Chem., 27, 3–18, for a full discussion of this matter.

[5] Compare Bein, Ztschr. physik. Chem., 27, 21, in regard to the source of error arising from the deposition of small quantities of basic salt on the anode.

equally satisfactory method described for preventing the dispersion of the hydroxyl ions produced at the cathode,[3] and Hittorf, Bein, and others in their investigations have simply taken care to stop the electrolysis before the alkali had reached the middle portions.

This procedure is, however, open to the objection that the absolute amount of substance transferred is necessarily small, and since this small amount is obtained as a difference of two much larger experimentally determined quantities, the percentage errors in the final results are necessarily large. Thus in Bein's experiments on metallic chlorides, which are probably the most accurate with polarizable electrodes thus far published, the amount of chlorine transferred was in almost all cases between 9 and 40 milligrams, and this value was obtained by subtracting two quantities usually 4–10 times as great. It is true, to be sure, owing to the great accuracy of the volumetric determination of chlorine, that the corresponding transference values exhibit an average deviation from the mean of only 0.6–0.7 per cent.[2] This degree of accuracy could probably not be reached in the case of most other ions, and even it leaves very much to be desired.

It occurred to me now that the difficulty just considered, arising from the dispersion of the hydrogen and hydroxyl ions into the solution, might be entirely obviated by the simple device of gradually adding during the electrolysis to the solutions around the cathode and anode, sufficient amounts of the acid and base, respectively, of which the salt is composed, to keep those solutions neutral (or, preferably in practice, slightly acid and alkaline, respectively). If, furthermore, the acid and base added are dissolved in suitable quantities of water, it is evident that not only the formation of new substances around the electrode may be prevented, but also that the changes of concentration of the original salt due to transference may be compensated, so that the whole solution will remain unchanged in composition, and the electrolysis can be continued indefinitely. Thus, if the transference number (which is approximately 0.5) of a

[1] Both Lenz and Hopfgartner with this purpose in view, covered the cathode, which consisted of mercury, with concentrated zinc chloride solution, but this prevented an accurate analysis of the solution around the cathode.

[2] This estimate is based on a consideration of Bein's results with the chlorides of the alkali and alkaline-earth metals at ordinary temperatures (pp. 49–51 of his article).

0.2 normal potassium sulphate solution were to be determined, one would add gradually at the cathode 0.4 normal sulphuric acid in such (measured) amounts, determined with the help of an indicator or calculated from the electricity passing through, as will keep the solution slightly acid; and would add at the anode an equal amount of 0.4 normal potassium hydroxide. If, however, the transference number of the positive ion were 2/3 and the salt 0.2 normal as before, the acid solution used would have to be 0.3 and the base solution 0.6 normal, and the volume of the former added would have to be twice that of the latter, in order to keep the concentration constant. In practice, however, it is desirable that the added solutions should be somewhat stronger (or weaker) than the theory requires, in order to prevent the solution around the electrodes from rising (or sinking) into the middle portions.

Three salts, potassium sulphate, barium chloride, and barium nitrate, were investigated in the order in which they are here named, each one at two concentrations, 0.1 and 0.02 molar.[1] The samples used were prepared by recrystallizing the commercial chemically pure salts two or three times from water. In the case of the potassium sulphate, the analyses of the solutions, both before and after the electrolysis, were made by evaporating them, after exactly neutralizing, if necessary, with sulphuric acid, to dryness on a water bath in platinum dishes, and igniting the residue, at first very gently and then intensely. Great difficulty was experienced by reason of decrepitation on first heating; but this source of error was entirely removed by tying ash-free filter-paper closely over the top of the dish, heating carefully only the bottom of the dish so as to avoid igniting the paper, and afterwards incinerating the latter. In the case of the two barium salts, the analyses were made by adding a slight excess of sulphuric acid to the solution, evaporating to dryness as before, and igniting the residue to a constant weight at a moderate

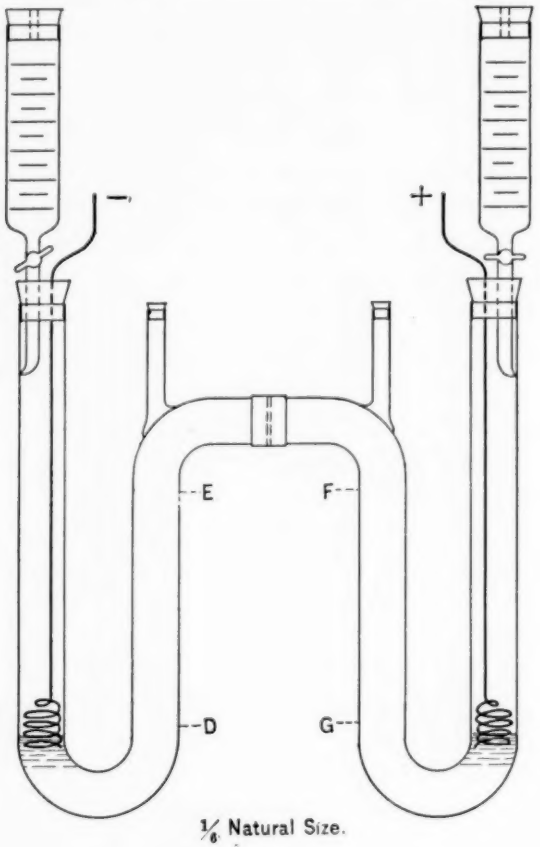
[1] I use this term (previously suggested by Ostwald) to designate the concentration of solutions containing one mol (one molecular weight in grams) in one liter of solution. The general introduction of some such term seems highly desirable, first in order to avoid a very frequently occurring circumlocution, and second, in order to avoid the serious confusion which is beginning to arise through the double use, by some writers, of the term *normal*, namely its use in this sense, as well as in its appropriate sense of one equivalent per liter.

red heat. During the evaporation, the dishes were covered with filter-paper (which was afterward incinerated), in order to avoid a loss of the precipitate by spattering, occasioned by the escape of small bubbles of air from the solution. This subtle source of error caused, before it was discovered, the loss of several transference determinations. The barium hydroxide solution added at the anode was, in the case of the barium nitrate experiments, analyzed in just the same manner.

The method employed in carrying out the transference experiments with barium nitrate was somewhat different in its details from that used in the case of the other two salts. I will first fully describe the former method, for it has, I believe, some advantages over the latter; and will then briefly mention the respects in which the two methods differ.

At the beginning of each experiment, the apparatus, shown in the accompanying sketch, consisting essentially of two large glass U tubes, 3.5 cms. in diameter, joined by a piece of soft rubber tubing, was charged with such an amount of barium nitrate solution that the whole middle part of the U tubes and their side-arms up to a point about 2 cms. above the top of the bend were filled with it. Rubber stoppers were inserted in the small upright arms on the middle of the tube, so as to keep the solution in place. To the portions in the bends were added a few drops (a known weight) of phenolphthalein solution, in order to assist in regulating the addition of alkali and acid. The indicator is rapidly decolorized in the immediate neighborhood of the anode, but is nevertheless useful, since it retains its color in the bend beneath. Cork stoppers with one large and one small hole were inserted in the top of each side arm. Through the small holes passed heavy platinum wires bent at the bottom into the form of a spiral. These were made to dip only a few millimeters into the solution, and were gradually raised during the electrolysis so as to be always near the top of the liquid. The distance between the electrodes was 80 to 100 cm. Through the larger holes in the stoppers were inserted the stems of cylindrical drop-funnels, like those shown in the drawing. These were graduated with divisions corresponding to each 5 cc. The stems were bent slightly at their ends and drawn to a point, so as to

cause them to remain full of liquid and to deliver against the sides of the U tubes. These two drop-funnels were filled at the start with approximately 0.5 normal nitric acid[1] and barium hydroxide for the experiments with the more concentrated solution, and with



1/6 Natural Size.

Fig. 1.

0.1 normal acid and base for those with the more dilute. These funnels, which were closed above with one-hole rubber stoppers, were weighed to the nearest centigram before and after the electrolysis, the stems being capped with small test-tubes during the

[1] The acid solution used in the first experiments was prepared by diluting the concentrated acid with the pure distilled hydrogen peroxide solution, in order to entirely prevent reduction of the nitrate to nitrite and ammonia; but this precaution was later dispensed with, as it was found to make no difference in the results.

weighing. The base solution was protected from the air during the electrolysis by a soda-lime tube inserted in the rubber stopper.

At least twenty minutes before the electrolysis was started, the U tubes were immersed in a large thermostat at 25°, to such a depth that the middle horizontal part of the apparatus was entirely covered. After the temperature differences had become equalized, 2.5 cc. of the nitric acid solution were added at the cathode and 10 to 15 cc. of the barium hydroxide solution at the anode. This excess of the latter was added at the start, in order to make the anode solution distinctly heavier than the middle portion above, and to introduce into the bend enough free base to neutralize any acid which might escape neutralization in the immediate neighborhood of the electrode. The electrodes were then connected through a switch, two 32-candle-power lamps, a Weston milliammeter, and a silver voltameter, all in series, with the terminals of the city-circuit of 110 volts potential; and the current was turned on. The silver voltameter consisted of a platinum dish (serving as cathode) which contained a 15 per cent. silver nitrate solution, just beneath the surface of which was placed a horizontal silver plate (to serve as anode) which was wrapped with filter paper and supported by a silver rod riveted through it. The milliammeter served merely to indicate the strength of the current, and was not used for a quantitative determination of it.

As the electrolysis proceeded, at intervals of 10–12 minutes, each time as soon as the pink color appeared at the cathode, 2.5 cc. of the nitric acid and an equal volume of the barium hydroxide solution were added. The electrolysis was continued for about three hours. At the end of this time the electrodes and drop-funnels were removed, perforated rubber stoppers were inserted in the side arms, their holes were closed by pushing in pieces of glass rod, and the stoppers in the small middle arms were taken out. Through these arms three middle portions (lying between the points E and F, D and E, and F and G in the figure) were slowly removed by means of a pipette connected with a suction pump, the tip of the pipette being gradually lowered so as to be always just beneath the surface of the liquid; the portions were then transferred to small flasks. The apparatus was next removed from the thermostat

and separated at the rubber band; the U tubes were wiped off outside with a dry cloth, the liquid on the inside adhering to the upper part of the middle arms being also removed; and the tubes were weighed separately on a large balance, after adding to the anode portion a weighed amount of dilute nitric acid sufficient to make the solution acid, thus avoiding later the absorption of carbon dioxide from the air. The contents of the U tubes were now transferred as completely as possible to small flasks, the liquid being once poured back to secure thorough mixing. The U tubes were then washed out, dried, and weighed. The flasks were all weighed, their contents poured out into the platinum dishes, and the nearly empty flasks again weighed. The weights of barium sulphate obtained from the cathode and anode portions were corrected for the small known weights of solution remaining in the U tubes.

In the case of the potassium sulphate and barium chloride experiments, only the cathode and middle portions were analyzed. The method of conducting the electrolysis was also somewhat different in these cases. The side-arms of the U tubes were at the beginning filled with solution for two-thirds of their length (instead of up to a point only a little above the bends) and the concentrations of the acid and base solutions added were made ten per cent. less (instead of greater) than would be required to maintain a constant concentration, in order to prevent the portions around the electrodes from sinking into the unchanged solution beneath. These solutions were added from burrettes with tips turned upward and delivering a little below the bottom of the electrodes, which reached as before just beneath the surface of the liquid. The weight of the sulphuric or hydrochloric acid solution added was calculated from the measured number of cubic centimeters with the help of the known specific gravity of the solution; this volume measurement is unobjectionable in the case of the acid solution added, since no non-volatile matter is introduced, and the greatest accuracy is therefore not required, but direct weighing of the base solution is far preferable in case the anode portion is to be analyzed. Both methods of charging the U tubes and of regulating the concentration at the electrodes give satisfactory results; in that last described, the middle portion is of greater length, and the electrolysis could

perhaps be longer continued, if it were desired to do so. The method used in the case of the barium nitrate is preferable, however, when the base solution to be added, like that of barium hydroxide, is heavy; for, if the other method is used, it is difficult to prevent the added portions from sinking down before they become mixed with the liquid already surrounding the electrode. The electrolyses of the potassium sulphate and barium chloride solutions were continued from four to eight hours.

4. Results of the Transference Determinations.

The experimental data and the calculated transference numbers are given in the tables below. All the values given (except, of course, the current, time, and transference numbers) are weights in grams. Those in the columns relating to the salt-content are the quantities of the substances actually weighed, namely of the potassium sulphate and barium sulphate. In the second column, the portion of the solution surrounding the cathode is designated by K, the adjoining middle portion by M_I, the next one by M_{II}, that adjoining the anode portion by M_{III}, and the anode portion itself by A.

The temperature was in all cases 25°.

The original solutions submitted to electrolysis, the concentrations of which are only approximately stated in the headings, were found to contain the following amounts of salt in 1000 grams of *solution:* in experiments, nos. 1 and 2, 17.247 gms.; in no. 3, 17.205 gms.; and in nos. 4, 5, and 6, 3.4927 gms. K_2SO_4: in nos. 7, 8, 9, and 10, 22.906 gms.; in nos. 11, 12, and 13, 4.6448 gms.; in nos. 14, 15, and 16, 21.083 gms.; in no. 17, 21.099 gms.; in nos. 18 and 19, 4.6666 gms., and in no. 20, 4.6560 gms. $BaSO_4$. The barium hydroxide solution added in experiments 14, 15, 16, and 17 gave 56.443 gms. $BaSO_4$, and that used in experiments 18, 19, and 20, gave 11.700 gms. $BaSO_4$ for 1000 gms. of solution.

The values of the transference numbers, which are given in the last columns of the tables, are those of the positive ions multiplied by 100. The way in which these were calculated may be illustrated with the help of the data obtained in the first experiment with potassium sulphate (see the table below). The cathode portion submitted to analysis weighed 493.12 grams, and was found to contain 8.4394 grams K_2SO_4. To determine what it contained before

the electrolysis, we must evidently subtract from the final weight of the portion, the weight of all matter which was introduced in the process of carrying out the electrolysis, and multiply the remainder by the original salt-content, which was 0.017247 gm. per gram of solution. The weight of dilute sulphuric acid and phenolphthalein added, which was 60.78 grams in this experiment, must therefore be first subtracted. Secondly, a correction must be made for the fact that the weight of the cathode portion is, by the electrolysis itself, increased by the weight of the potassium ions which have migrated into it, and decreased by the weight of sulphate ions which have migrated out of it[1] and by the weight of the hydrogen gas which escaped at the electrode. Since the average value of the transference number is found to be 0.493, the total increase of weight from these three causes would evidently be: $(39.1 \times 0.493) - (48.0 \times 0.507) - 1.0 = -6.0$ gms., for every 108 gms. of silver deposited in the voltameter, or -0.14 gm. in this experiment. The increase in the amount of the salt in the cathode portion is therefore $8.4394 - (493.12 - 60.78 + 0.14)\,0.017247 = 0.9803$ gms. Adding to this the change ($+0.0013$) in the adjoining portion and dividing by the equivalent weight of potassium sulphate (87.18), and by the number of equivalents of silver precipitated in the voltameter, the transference number is found to be 0.4941. The cases where the adjoining portion suffered a change in concentration greater than the analytical error, and where consequently this change was combined with that of the cathode or anode portion are indicated in the table by a brace following the two quantities. The calculation of the transference number from the change in concentration at the anode was, in the case of the barium nitrate experiments, made in an entirely analogous manner, except that from the weight of barium sulphate obtained from the anode portion after the electrolysis, there was of course subtracted the amount coming from the barium hydroxide solution added. For the sake of greater clearness, the total weight of salt obtained from the anode portion is, in the table, resolved into the two corresponding components.

[1] It is evidently assumed hereby, as is always done in transference calculations, that the ions are not hydrated. It may not be without value to call attention to the fact that the commonly observed change of the calculated transference numbers with the concentration may be due, wholly or in part, in the case of concentrated solutions, to hydration of the ions, and to the failure to take this into account in the calculation.

Potassium Sulphate, 0.1 *molar*.

Expt. No.	Portion	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
1	K	493.12	8.4394	60.78	7.4591	+0.9803	2.4594	49.41
	M_I	137.47	2.3723		2.3710	+0.0013	0.11 amp.	
	M_{II}	204.82	3.5365		3.5326	+0.0039	310 min.	
2	K	456.48	7.7762	91.21	6.3033	+1.4729	3.6760	49.33
	M_I	175.15	3.0126		3.0209	−0.0083	0.134 amp.	
	M_{II}	86.96	1.4993		1.4998	−0.0005	415 min.	
3	K	434.79	7.4142	48.70	6.6446	+0.7696	1.9370	49.19
	M_I	119.85	2.0615		2.0620	−0.0005	0.063 amp.	
	M_{II}	133.38	2.2941		2.2948	−0.0007	460 min.	

Potassium Sulphate, 0.02 *molar*.

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
4	K	491.47	1.6964	56.73	1.5185	+0.1779	0.4451	49.68
	M_I	103.75	0.3631		0.3624	+0.0007	0.028 amp.	
	M_{II}	102.99	0.3599		0.3597	+0.0002	240 min.	
5	K	463.31	1.5869	84.31	1.3238	+0.2631	0.6524	49.59
	M_I	176.04	0.6131		0.6149	−0.0018	0.040 amp.	
	M_{II}	94.08	0.3289		0.3286	+0.0003	245 min.	
6	K	469.56	1.6246	57.40	1.4397	+0.1849	0.4617	49.58
	M_I	103.17	0.3604		0.3603	+0.0001	0.018 amp.	
	M_{II}	107.24	0.3745		0.3746	−0.0001	380 min.	

Barium Chloride, 0.1 *molar*.

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
7	K	460.04	10.6238	30.33	9.8402	+0.7836	1.7479	41.44
	M_I	46.30	1.0598		1.0605	−0.0007	0.108 amp.	
	M_{II}	99.09	2.2686		2.2697	−0.0011	240 min.	
8	K	512.08	11.9214	57.06	10.4182	+1.5032	3.3519	41.46
	M_I	35.77	0.8189		0.8193	−0.0004	0.122 amp.	
	M_{II}	104.51	2.3911		2.3939	−0.0028	410 min.	
	M_{III}	99.00	2.2673		2.2677	−0.0004		
9	K	507.37	11.7885	50.98	10.4500	+1.3385	2.9804	41.48
	M_I	106.63	2.4411		2.4424	−0.0013	0.123 amp.	
	M_{II}	101.06	2.3116		2.3149	−0.0033	360 min.	
	M_{III}	90.10	2.0615		2.0638	−0.0023		
10	K	474.93	10.8589	30.31	10.1824	+0.6765	1.5019	41.50
	M_I	103.15	2.3604		2.3628	−0.0024	0.065 amp.	
	M_{II}	108.48	2.4821		2.4848	−0.0027	345 min.	
	M_{III}	85.59	1.9574		1.9605	−0.0031		

Barium Chloride, 0.02 *molar*.

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
11	K	514.75	2.3897	54.95	2.1354	+0.2543	0.5321	44.31
	M_I	110.70	0.5149		0.5142	+0.0007	0.034 amp.	
	M_{II}	115.31	0.5362		0.5366	+0.0006	230 min.	
	M_{III}	89.89	0.4175		0.4175	0.0000		
12	K	499.37	2.3214	50.15	2.0864	+0.2350	0.4928	44.19
	M_I	110.59	0.5142		0.5137	+0.0005	0.022 amp.	
	M_{III}[1]	86.12	0.4007		0.4000	+0.0007	275 min.	
13	K	493.42	2.2930	49.84	2.0601	+0.2329	0.4885	44.16
	M_I	106.63	0.4957		0.4953	+0.0004	0.023 amp.	
	M_{II}	109.52	0.5089		0.5087	+0.0002	260 min.	
	M_{III}	95.84	0.4451		0.4452	−0.0001		

Barium Nitrate, 0.1 *molar*.

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
14	K	244.30	5.2507	40.53	4.2970	+0.9537	1.9334	45.54
	M_I	180.57	3.8058		3.8070	−0.0012	0.175 amp.	
	M_{II}	199.75	4.2106		4.2212	−0.0006	165 min.	
	M_{III}	239.02	5.0368		5.0388	−0.0020		
	A	205.23	2.5491		3.5000	−0.9509		45.56
			2.2196	39.325				
15	K	269.42	5.8130	43.89	4.7562	+1.0568	2.1540	45.47
	M_I	174.74	3.6864		3.6840	+0.0024	0.178 amp.	
	M_{II}	174.33	3.6760		3.6753	+0.0007	180 min.	
	M_{III}	183.50	3.8710		3.8685	+0.0025		
	A	218.25	2.5877		3.6497	−1.0620		45.48
			2.5527	45.233				
16	K	268.51	5.7520	44.355	4.7270	+1.0250	2.0917	45.46
	M_I	172.63	3.6428		3.6395	+0.0033	0.173 amp.	
	M_{II}	147.53	3.1110		3.1098	+0.0002	180 min.	
	M_{III}	157.03	3.3132		3.3100	+0.0032		
	A	204.41	2.1725		3.2065	−1.0340		45.56
			2.9600	52.44				
17	K	278.03	5.8841	46.49	4.8846	+0.9995	2.0301	45.54
	M_I	168.20	3.5492		3.5488	+0.0004	0.168 amp.	
	M_{II}	158.30	3.3329		3.3326	+0.0003	180 min.	
	M_{III}	153.30	3.2360		3.2345	+0.0015		
	A	205.69	2.4465		3.4451	−0.9986		45.42
			2.3988	42.50				

[1] Portion M_{II} was lost in this experiment.

Barium Nitrate, 0.02 *molar*.

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
18	K	197.50	1.0234	20.88	0.8242	+0.1992	0.4042	45.57
	M_I	122.58	0.5744		0.5744	±0.0000	0.033 amp.	
	M_{II}	134.06	0.6267		0.6269	−0.0002	180 min.	
	M_{III}	187.20	0.8143		0.8150	−0.0007		
	A	253.88	0.7158		0.9149	−0.1991		45.70
			0.6766	57.83				
19	K	207.34	1.0631	21.75	0.8660	+0.1971	0.4014	45.41
	M_I	124.05	0.5773		0.5772	+0.0001	0.033 amp.	
	M_{II}	141.65	0.6608		0.6610	−0.0002	180 min.	
	M_{III}	145.38	0.6781		0.6772	+0.0009		
	A	268.13	0.7979		0.9971	−0.1992		45.68
			0.6371	54.45				
20	K	201.18	1.0346	21.14	0.8382	+0.1964	0.3985	45.57
	M_I	123.27	0.5630		0.5630	±0.0000	0.035 amp.	
	M_{II}	121.00	0.5641		0.5640	+0.0001	170 min.	
	M_{III}	155.48	0.7240		0.7239	+0.0001		
	A	279.26	0.8353		1.0329	−0.1976		45.85
			0.6716	57.40				

The values of the transference numbers obtained (multiplied by 100) are summarized in the following table. At the foot of each column is given the mean of the values just above, and the average deviation of the separate values from this mean. To the final results in the case of the barium nitrate, the probable error, calculated in the usual manner, is appended.

Potassium Sulphate.		Barium Chloride.	
0.1 molar.	0.02 molar.	0.1 molar.	0.02 molar.
49.41	49.68	41.44	44.31
49.33	49.59	41.46	44.19
49.19	49.58	41.48	44.16
		41.50	
49.31	49.62	41.47	44.22
0.08	0.04	0.02	0.06

Barium Nitrate.			
0.1 molar.		0.02 molar.	
Cathode Values.	Anode Values.	Cathode Values.	Anode Values.
45.54	45.56	45.57	45.70
45.47	45.48	45.41	45.68
45.46	45.56	45.57	45.85
45.54	45.42		
45.50	45.50	45.52	45.74
0.04	0.06	0.07	0.07
45.50 ±0.02		45.59 ±0.08	

5. ACCURACY OF THE RESULTS.

The probable degree of accuracy of the results and the consequent reliability and value of the method employed may be next considered. It should be first stated that in the above tables all the determinations are recorded which were carried to completion after certain errors which were found to exist in the analyses were eliminated.

In the cases of potassium sulphate and barium chloride, there are two indications of the degree of accuracy of the results; first, the change in weight of the middle portions; and second, the variations in the transference-values calculated from the different experiments. In regard to the former, it should be stated that in the analyses of portions of the original solutions, variations from the mean salt-content of 0.0010 gm. in the more concentrated, and of 0.0005 gm. in the more dilute solution, were found to exist; so that only when the middle portions change by more than these amounts, do the changes have much significance. It will be seen that the changes in the M_I portions do not much exceed these amounts, except in the cases of experiments 2, 5, and 10; and in the first two of these experiments, the changes in the M_{II} portions are so small as to cause no hesitation in combining the changes of the M_I portions with those of the cathode portions. It will also be seen from the summary in the last table, that the average deviation of the separate transference values from the mean is in every case less than 0.2 per cent. Taking into account the possibility of an error of 0.1 per cent. in the determination of the original salt-content, it can, I think,

be safely asserted that it is almost certain that the error in the mean transference values does not exceed 0.25 per cent.; in other words, the third figure cannot be in error by more than one unit. The probable error is, of course, much less.

In the case of the barium nitrate experiments, a more conclusive confirmation of the degree of accuracy of the results is furnished by a comparison of the cathode and anode values; for an error in the determination of the original salt-content of the solution or any error arising from mechanical loss in the analysis of the portions would affect these values in the opposite direction. In the case of the 0.1 molar solutions, the agreement is complete between the mean cathode and anode values. Taking into account, moreover, the smallness of the variations of the separate values of the mean, and the slight changes (0.2–0.7 mgm.) exhibited by the M_{II} portions, the final result (45.50) can, I believe, be regarded as almost surely accurate to 0.1 per cent. of its value. In the case of the 0.02 molar solution, the values calculated from the changes at the two electrodes differ by a little less than half a per cent. Attributing double weight to the cathode results, since an increase of the salt-content is produced by the base solution added at the anode, I adopt 45.59 as the most probable value. This may possibly be in error by 0.3 per cent., but is probably accurate to one-half that amount. Since at both concentrations, the final values are derived by a combination of the results of two independent methods which are liable to error in opposite directions, the probable errors given in the table are to be regarded as a measure, not merely of the variable errors, but probably of all errors involved.

These considerations show that the degree of accuracy attained with the help of the method described in this article is much greater than that which it has heretofore been found possible to secure. This arises mainly from the fact that the electrolysis could be continued until a much larger weight of salt was transferred. Thus, in my experiments, the quantities transferred were 180–260 mgms. in the 0.02 molar, and 700–1500 mgms. in the 0.1 molar solution, while, in Bein's determinations at corresponding concentrations, only 20–50 mgms. were transferred.

6. COMPARISON WITH EARLIER RESULTS.

Potassium sulphate was investigated by Hittorf[1] at 4°–12° at two concentrations, at about 0.5 and about 0.014 molar. The transference numbers found were 0.500 and 0.498, respectively. The differences from my values (0.4931 and 0.4962) are, therefore, not very large.

Barium chloride has been studied by various investigators with widely divergent results. Thus Hittorf[2] obtained the value 0.385 at 10°–20° for 0.04–0.06 molar solutions; while from Bein's results,[3] one finds by interpolation for 25° and 0.1 and 0.02 molar concentrations, the values 0.424 and 0.445, respectively. The latter differ by 2.2 and by 0.7 per cent., respectively, from those presented in this article (0.4147 and 0.4422). Hopfgartner's[4] determinations (at 15°) for a 0.1 molar solution, lead to the value 0.408 which is nearly as much below my result as Bein's is above it.

Barium nitrate has been investigated only by Hittorf,[1] who found 0.380 in 0.07, and 0.398 in 0.03 molar solution. These values differ very widely from my own (0.455).

These results make evident the great need of a repetition of much of the earlier work on tri-ionic salts.

7. CHANGE OF THE TRANSFERENCE NUMBERS WITH THE CONCENTRATION.

The effect of concentration, the study of which formed the main object of this investigation, may be now considered.

The transference number of potassium sulphate varies only from 0.4931 to 0.4962, or about 0.6 per cent., between the concentrations of 0.1 and 0.02 mols per liter. A little consideration will show that this change can be explained by assuming that 1.2 per cent. more of the dissociated part of the salt is dissociated into $K^{\cdot}$ and KSO_4' ions in the concentrated than in the dilute solution, it being further assumed, as a sufficiently close approximation, that the equivalent conductivities of all the ions involved are equal. But,

[1] Ostwald's Klassiker, No. 21, 58; or Pogg. Ann., 98, 29, 30.
[2] Ostwald's Klassiker, No. 23, 41; or Pogg. Ann., 106, 380, 381.
[3] Ztschr. phys. Chem., 27, 51.
[4] Ztschr. phys. Chem., 25, 138.

since, according to Kohlrausch's measurements, the molecular conductivity between these two concentrations changes from 175 to 208 reciprocal ohms (and the dissociation from 64.5 to 77 per cent.), thus by 19 per cent., it is clear that by far the most important chemical change produced by the dilution is the dissociation of K_2SO_4 molecules and not of KSO_4' ions. Since the change in the transference number is so small, it may, however, be due solely to hydration of the ions.[1] Therefore, only the following negative conclusion is justifiable: *the concentration of KSO_4' ions[2] in a 0.1 molar potassium sulphate solution does not exceed a very few per cent. of the total concentration.* If these ions exist at all, they have a very much greater dissociation-tendency than the neutral potassium sulphate molecules.

In the case of barium nitrate, the change (0.2 per cent.) caused by the five-fold dilution is still smaller, and does not exceed the probable experimental error. Therefore, *barium nitrate solutions up to 0.1 molar concentration contain in appreciable quantity only $Ba^{\cdot\cdot}$ and NO_3' ions and no complex ions formed by the combination of these.*

The difference in the transference numbers (0.4147 and 0.4422) of barium chloride at the two concentrations is very much greater than the differences just considered, amounting as it does to 6.6 per cent. The change is, moreover, in the opposite direction from that required by the assumption of the existence of $BaCl^{\cdot}$ ions in the more concentrated solution. In order to explain this behavior and the analogous one of strontium and calcium chlorides, Bein assumed a partial hydrolysis of the salt, basing this view on the disagreement of a single determination of the amount of calcium transferred with determinations of the chlorine transferred. This explanation can not, however, be correct, since the alkaline-earth hydroxides are known to be very strong bases; it is, moreover, entirely disproved in the case of barium chloride, by the substantial agreement (see § 6) of Bein's values, which are based on determinations

[1] Ostwald's Klassiker, No. 23, 41; or Pogg. Ann., 106, 378, 379.

[2] Thus the actual change of 0.6 per cent. would be entirely accounted for, if, with the equivalent weight of the $K^{\cdot}$ ions, migrate two molecules of water more than migrate with the equivalent weight of SO_4'' ions.

of the chlorine transferred, with my results, which were obtained by determining the transferred barium. On the contrary, the behavior of these chlorides of the alkaline-earth metals is entirely similar to that of the halogen compounds of cadmium, though the anomaly is less pronounced; and, as far as I am able to see, it admits only of a corresponding explanation. In order to account for the fact that the sum of the transference numbers for the metal and chlorine is equal to unity, and for the change with the dilution, it is, namely, necessary to assume that *there are present in considerable quantity in the 0.1 molar solution of the alkaline-earth chlorides, complex negative ions formed by the union of one or more chlorine ions with one or more of the chloride molecules* (such ions, for example, as $BaCl_3'$ or $BaCl_4''$) and that these ions dissociate with increasing dilution.

8. RATES OF MIGRATION OF THE BIVALENT IONS.

As Kohlrausch has pointed out, owing to the lack of exact transference values for tri-ionic salts, the Law of the Independent Migration of the Ions has not been satisfactorily confirmed in the case of bivalent ions; nor have their rates of migration, calculated with the help of that Law, been as accurately determined as have those of univalent ions, for the reason just mentioned, and also for the reason that the limiting value of the molecular conductivity of tri-ionic salts cannot be established with as great certainty, since a larger extrapolation is necessary.

With the help of the new transference numbers for potassium sulphate and barium nitrate, the equivalent conductivities of the SO_4'' and $Ba^{\cdot\cdot}$ ions can be calculated, if it be assumed that the values obtained for 0.02 molar solution at 25° would also hold true for extreme dilution and at 18°. That these assumptions will not give rise to an error greater than one per cent. is highly probable in view of the small changes between the two concentrations, 0.1 and 0.02 molar, and in view of the general principle that temperature has as a rule only a small effect on transference numbers. The calculation can be made in two ways, either by combining with my transference numbers the conductivities at extreme dilution of the $K^{\cdot}$ and NO_3' ions, which have been derived by Kohlrausch through a con-

sideration of the transference numbers and the molecular conductivities of di-ionic salts; or by combining with them the limiting values of the equivalent conductivities of potassium sulphate and barium nitrate. The results so obtained for the SO_4'' and $Ba^{\cdot\cdot}$ ions can be then further compared with Kohlrausch's values which were derived by a combination of the two kinds of data last mentioned, without reference to the transference number of any tri-ionic salt.[1]

The three pairs of calculated values of the equivalent conductivities of the two ions are given below in the order in which they have just been referred to. The data used in the calculation are the transference numbers recorded above (0.4962 for K_2SO_4 and 0.4559 for $Ba(NO_3)_2$) and the following values of the equivalent conductivity expressed in reciprocal ohms at extreme dilution;[2] for $K^{\cdot}$, 64.8; for NO_3', 61.3; for K_2SO_4, 135.5; and for $Ba(NO_3)_2$, 119.3.

	I	II	III
SO_4''	65.8	68.3	69.7
$Ba^{\cdot\cdot}$	51.4	54.4	57.3

The difference between the three pairs of values are by no means inconsiderable. In the case of the $Ba^{\cdot\cdot}$ ion, indeed, the first and third methods of calculation give results differing by over 10 per cent. Aside from serious errors in the experimental data, these differences may be due to one or more of the three following causes: first, error in the conductivity values calculated for the univalent ions; second, error in the extrapolated values for the univalent conductivity at extreme dilution of the tri-ionic salts; and third, inaccuracy in the assumption that the transference numbers for potassium sulphate and barium nitrate at extreme dilution do not differ much from those found in 0.02 and 0.1 molar solution. It seems very improbable that any one of these three errors can be large enough to account for the divergences; a combination of them, however, may possibly do so. In the absence of definite information in regard to the matter, it seems best to adopt provisionally the values given in column II ($SO_4'' = 68.3$; $Ba^{\cdot\cdot} = 54.4$) which are the ones most directly derived from experimental data, and which are not far

[1] Wied. Ann., 66, 805.

[2] These values are those given by Kohlrausch, Wied. Ann., 66, 795 and 819, 812 and 804.

from the means of the other two pairs of values. These numbers give for the equivalent conductivities of potassium sulphate and barium nitrate, 133.1 and 115.7 respectively, while Kohlrausch's extrapolated values are 135.5 and 119.3.

In this connection it should be pointed out that in Kohlrausch's method of treatment of tri-ionic salts, the assumption involved that the conductivity of bivalent ions decreases with increasing concentration more rapidly than that of the univalent ions simultaneously present, is entirely inconsistent with the transference results on potassium sulphate and barium nitrate presented in this article. This is shown by the following transference numbers which are calculated for these two salts from his values for the separate ions at the various normal concentrations, which are stated below in the headline :

	0.1	0.05	0.02	0.01	0.001
K_2SO_4	0.571	0.557	0.534	0.522	0.499
$Ba(NO_3)_2$	0.397	0.414	0.434	0.446	0.468

It is certain from my results that any such change of the transference numbers with the concentration is out of the question in the case of these two salts. It ought to be added that Kohlrausch regarded his assumption only as a provisional one, having an empirical justification. That the results obtained with its help were at all satisfactory is probably due, first, to the fact that the compounds considered were mostly those of the halogens, and secondly, to the large errors in some of the transference numbers.

It is impossible to utilize the transference numbers of barium chloride, as was done with those of the nitrate, for the calculation of the conductivity of the barium ion, since the transference number of the former salt does change greatly with the dilution. It is of interest, however, to make the converse calculation so as to compare the transference number calculated for extreme dilution with that found at the concentrations investigated. Assuming as above, $Ba^{\cdot\cdot} = 54.4$, and according to Kohlrausch, $Cl' = 66.4$, the transference number for complete dissociation is found to be 0.450. (Even

assuming Kohlrausch's much higher value (57.3) for the $Ba^{\cdot\cdot}$ ion, the transference number becomes only 0.464). The value found for a 0.02 molar solution was 0.442, so that the change produced by further dilution is relatively small. At this concentration, therefore, the complex negative ions present in considerable quantity in more concentrated barium chloride solutions, are for the most part, dissociated.

In closing, I desire to state that the accuracy of the experimental results present in this article are to be attributed in large measure to the analytical skill and perseverance of my assistants, Mr. A. A. Blanchard and Mr. G. V. Sammet.

DETERMINATION OF POISSON'S RATIO BY MEANS OF AN INTERFERENCE APPARATUS.

BY J. R. BENTON.

POISSON proved that when a homogeneous isotropic body is extended in one direction, it must contract in the directions perpendicular to the extension, and that if the intermolecular forces are assumed equal in all directions, the contraction must amount to ¼ of the extension. Numerous experiments, embracing a great variety of methods, have shown that this contraction actually does take place, but that the ratio in which it stands to the extension—Poisson's ratio—is usually different from ¼. This is accounted for under the assumption of imperfect homogeneity; indeed the ratio varies greatly for the same material according to the manner in which it has been treated. Voigt,[1] experimenting on electrolytically deposited copper, where there is no reason to expect inhomogeneity, found the ratio to have almost exactly its theoretical value of ¼.

The methods of determining Poisson's ratio may be divided into two classes.

First, those which depend on a comparison of the elastic constants of the medium investigated. It can be shown that Poisson's ratio K satisfies the equation:

$$K = \frac{B}{A + 2B}$$

where A and B are fundamental elastic constants of the medium. A and B can be determined from the behavior of the medium with respect to two different kinds of deformations, such as extension and flexure. Thus extension and torsion were used by Kohlrausch and Loomis,[2] and by Baumeister[3] to determine K; flexure and torsion

[1] W. Voigt: Berliner Sitzungsberichte, 1884, p. 961; 1884, p. 1004.
[2] Poggendorff's Annalen, Band 141, p. 502, 1870.
[3] Wiedemann's Annalen, Band 18, p. 578, 1883.

by Voigt,[1] Kirchhoff[2] and Okatow,[3] while Amagat[4] compared with other deformations cubical contraction under increase of pressure. Schneebelli[5] compared the velocity of torsional and longitudinal vibration of metal rods. Cornu[6] used an ingenious method in investigating Poisson's ratio for glass; one piece of glass was slightly bent by means of weights, and another piece was laid on it; the resulting interference bands had the form of hyperbolas, and it can be shown that the tangent of the angle between the asymptotes of the hyperbolas and the axis of the glass plate is equal to Poisson's ratio.

Second, Poisson's ratio may be determined by measuring the contraction at right angles to the direction of the extension, and comparing it with the extension. The former of these quantities is very small, and has to be measured indirectly, unless the stretched body is a very thick rod, in which case larger forces than are usually available have to be applied to produce an appreciable extension. The problem reduces itself, therefore, to that of the measurement of a very small distance.

The first determination, carried out by Cagniard de la Tour[7] to test Poisson's theoretical result, was made by stretching a wire contained in a narrow tube filled with water. The contraction of the wire was calculated from the change of level of the water. A similar method was employed by Wertheim,[8] who made important investigations of Poisson's ratio; he filled a hollow cylinder, communicating with a capillary tube, with water; when the cylinder was stretched, the change of its volume could be determined from the change of level of the water in the capillary tube, and from this Poisson's ratio was obtained. Both these methods were unsatisfactory, because the apparatus acted like delicate thermometers, a very slight change of temperature of the large mass of water making a great difference in its level in the narrow tube.

[1] W. Voigt, Wiedemann's Amalen, Band 15, p. 497, 1882.
[2] Pogg. Annalen, Band 108, p. 369, 1859.
[3] Pogg. Annalen, Band 119, p. 11, 1863.
[4] Comp. Rend., 21, July, 1884.
[5] Pogg. Annalen, Band 140, p. 589, 1870.
[6] A. Cornu, Comptes Rendus, Tome 69, p. 333, 1869.
[7] Ann. Chim. Phys., Tome 36, p. 384, 1827.
[8] Ann. Chim. Phys., 3 ser., Tome 23, p. 52.

Measurements by means of the microscope have been made by Mallock,[1] who determined the change in distance between points marked on a rod, when the rod was bent. Direct measurement of the contraction has been made in cases where the deformation was very great; thus Röntgen[2] determined Poisson's ratio for caoutchouc by stamping a circle on a stretched band; when the tension was removed the circle became an ellipse whose axes furnished the necessary data for the determination.

At the suggestion of Professor Voigt, I undertook the measurement of the contraction by means of interference bands. The experiments were made in his laboratory in the University of Göttingen.

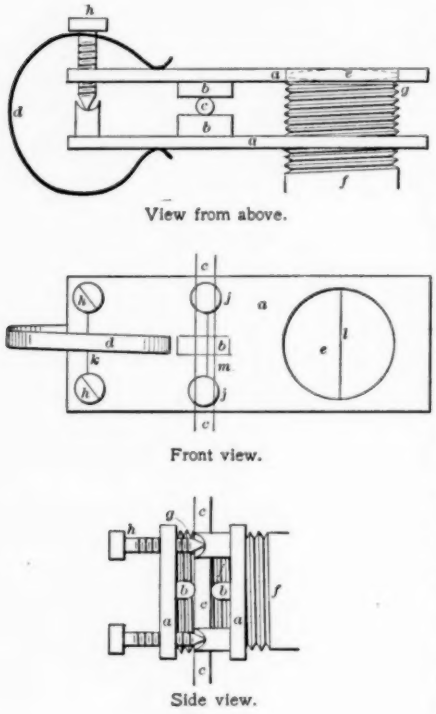


Fig. 1.

The interference of light has been already used to determine Poisson's ratio. Stromeyer and Kennedy[3] made use of it to measure the contraction of thick metal bars which were stretched in a testing machine. My apparatus is designed for use where such large forces are not available.

After making attempts with numerous variations of the apparatus, the following was found to give the most satisfactory results. *a*, *a* (Fig. 1) were plates of brass, on which the rounded bits of steel *b*, *b* were soldered, and firmly pressed against the wire *c* by means of the spring *d*. One plate contained a lens *e*, of slight curvature, the other a tube *f*, having a screw thread so that the distance of the glass

[1] Proc. Roy. Soc., vol. 29, p. 157, 1879.
[2] Poggendorff's Annalen, Band 157, p. 601, 1876.
[3] Proc. Roy. Soc., vol. 55, pp. 373–383, 1894.

plate g in its end from the lens could be adjusted. The back side of the glass plate g was blackened. By means of the screws h, h it was possible to set the plate perpendicular to the axis of the lens; in which case interference rings appeared, provided the distance between lens and plate was not too great. If the wire contracted, the distance became less, and new rings appeared. If sodium light is used, each new ring corresponds to a difference of distance of 294.5×10^{-6} mm., the half wave length of the light. This difference is not, however, itself the contraction of the wire, but the latter must be deduced from it when the distance of the wire and the center of the interference rings from the axis are known, around which the brass plates move. This axis is simply the line passing through the points of the screws h, h. In order to measure the distance from this axis, I ruled the fine lines k, l and m and measured accurately the distances kl and km, once for all. Then in any particular case the distances from l to the center of the rings, and from m to the center of the wire (seen through the holes jj) were measured by means of a microscope, and added to or subtracted from kl and km.

The wire was fastened above a table a (Fig. 2) and hung through a hole in it. b was a strong piece of iron. Underneath, the hook d, carrying the scale pan e, hung from a loop in the wire. A stiff iron rod f, free to move round the horizontal axis g, passed through a hole in the rod h and carried a weight l. The purpose of the weights e and l was simply to hold the wire tight, and to prevent f from slipping in the hole h. The weight by which the tension of the wire was produced, was applied to the end of f. The weight i wasplaced on a scale pan, which could be lowered by the windlass k so as to the rest on f, or raised from it; the purpose of this arrangement being to avoid jars in changing the weights. The interference apparatus was at m: in front of it was a Bunsen burner

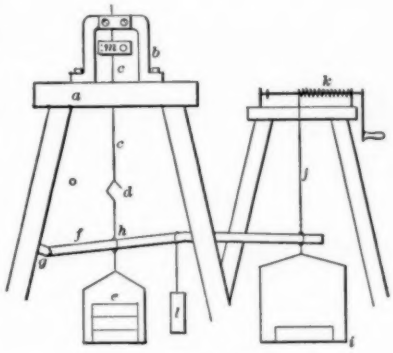


Fig. 2.

(not shown in the figure), in which a bead of Na_2CO_3 was held, and a microscope (also not shown), with which the rings were observed. The angle between the incident and the reflected ray was very small.

Each wire, after being fastened in the iron *b*, was heated to dull redness under a small load, by means of a Bunsen burner, in order to insure its hanging straight. Then it was left a day or two under a somewhat greater load than the one to be used in the experiments, after which the measurements were made.

The interference apparatus was placed on a wire, and the screws *hh* (Fig. 1), and the tube *f* so adjusted that the plate *g* was perpendicular to the axes of the lens, and very near to it, but yet not so near as to come into actual contact with it when the wire contracted. The cross-hairs of the microscope were set at first on the center of the rings which appeared under these conditions. Then the microscope was clamped in position, and the micrometer screw-head was turned until the intersection of the cross-hairs was on the tenth ring above the center. Here five readings of the micrometer were made, then the cross-hairs were brought on to the tenth ring underneath, where five readings were taken; then five readings were taken again on the tenth ring above. The difference between the average reading above and below gives the diameter of the tenth ring in terms of the divisions on the screw-head. Then the tension was brought to bear on the wire, the number of new rings counted, and the diameter of the tenth ring under these conditions was measured. Finally the tension was removed, another measurement of the diameter of the tenth ring was made, and also its difference from the diameter of the ninth ring and from that of the eleventh determined. The difference in diameter between the tenth ring with and without tension, divided by the difference in diameter between the tenth ring and the ring next to it, gives the fraction which must be added to the number of new rings in order to determine the change of distance between the plate and the lens. Suppose, for example, that the diameter (in terms of the divisions on the screw-head) of the tenth ring is 18.221 with tension, 18.005 without tension; that the average of the difference in diameter between the ninth and tenth and between the tenth and eleventh rings is 0.920; and that 4 new rings have appeared, then the distance through which the lens and plate have approached each other is

$$294.5 \times 10^{-6} \times \left(4 + \frac{18.221 - 18.005}{0.920}\right) = 1247 \times 10^{-6} \text{ mm.}$$

After making two such determinations at different places on the wire, it was loosened, turned through 90°, fastened again, heated to dull redness, and left hanging under a heavy load for a few hours. Then similar determinations were made at two different places on the wire, so that for each wire four determinations were made. The results given below are the averages of four such determinations each. The distance of the wire and rings from the screws *hh* (Fig. 1) was measured as described before; the weight *i* (Fig. 2) and the scale pan were weighed in a balance; the distance of the wire and the weight from the axis *g* were measured with a millimeter scale; and the diameter of the wire was measured with accurate calipers, the mean of six measurements being taken. From these quantities the contraction of the wire due to unit tension can be calculated.

Poisson's ratio is obtained by dividing this contraction by the extension due to unit tension. The last-named quantity was determined by measuring, with a micrometer, the vertical distance through which a needle point fastened to the end of the wire moved when weights were hung on the wire. For this purpose a 3-meter length of wire was used.

The values of Poisson's ratio found for a number of wires are given in the following table:

Substance.	Diameter.	Poisson's Ratio.	Mean Value.
Steel.	0.685 mm.	0.276	
	1.405	0.275	0.2755
Iron.	0.948	0.294	
	1.578	0.282	0.288
Copper.	1.390	0.337	
	1.728	0.345	0.341
Nickel.	0.963	0.375	
	1.490	0.271	
Brass.	0.787	0.328	
	1.498	0.334	0.331
Nickelin.	0.978	0.406	
	1.397	0.399	0.403
German Silver.	1.005	0.313	
	1.592	0.429	
Bronze.	0.902	0.414	
Brass containing much copper.	0.996	0.300	

The highly unsatisfactory discordant results for nickel appear to be due to some difference in the physical condition of the two wires. I found that their specific gravities were somewhat different. Of course the experiments were repeated, as soon as the discrepancy was found, but the same results were obtained.

The difference between the two values for German silver is due to difference in the composition of the alloy for the two wires.

THE USE OF THE BICYCLE WHEEL IN ILLUSTRATING THE PRINCIPLES OF THE GYROSCOPE.

By Charles T. Knipp.

IN the gyroscope as ordinarily made the true oscillatory motion of the axis is not shown except for extremely slow speeds of the fly wheel and then only for a few seconds. The oscillations are damped by the friction of the supports, causing the precessional motion to become steady.[1] The form of the gyroscope that best shows the true motion of the axis is a gyroscopic pendulum of considerable length. When in the form of the balanced gyroscope, where the balance can readily be destroyed by shifting the weight, thus coverting it into a gyroscopic pendulum of short length, the ordinary construction enables the oscillations to be seen only for slow speeds and short intervals; while in the top they are, in the ordinary form of apparatus, never visible.

The study of the phenomena peculiar to the gyroscope is greatly simplified, and at the same time brought within the reach of all, by using an ordinary bicycle wheel as the fly-wheel. So simple is the apparatus and yet so effective that it was thought well to call attention to some of the salient points.

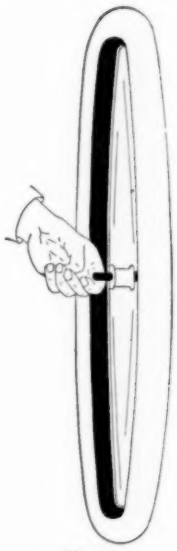


Fig. 1.

The bicycle wheel works equally well as a gyroscopic pendulum, as a balanced gyroscope, and as a top. It is readily mounted by any one who has access to a shop in which iron work is done, or any bicycle repair shop. The wheel is taken from the front fork without disturbing the adjustment of the ball bearings. A ⅜-inch iron gas pipe nine inches long is tapped out at one end and screwed on the axle of the wheel. The other end of the gas pipe, which is threaded to receive an ordinary connector, is slitted with a hack saw. The connector acts as a compression nut enabling the axis to be extended to any length by inserting an iron or brass rod.

[1] Merritt, Phys. Rev., vol. 14, p. 336, 1897.

Fig. 1 shows the wheel as when first taken from the bicycle. The axle extends beyond the hub far enough to give plenty of room for support. When spun and held as shown it furnishes a striking example of the familiar toy gyroscope. It is very positive in its precessional movements and seeming defiance to the laws of gravitation. In this form it is interesting to study its erratic movements when disturbed. This is best done by firmly grasping the ends of the axle with both hands and endeavoring to tilt the axle quickly while the wheel is turning. No doubt this simple experiment with the bicycle wheel is familiar to all.

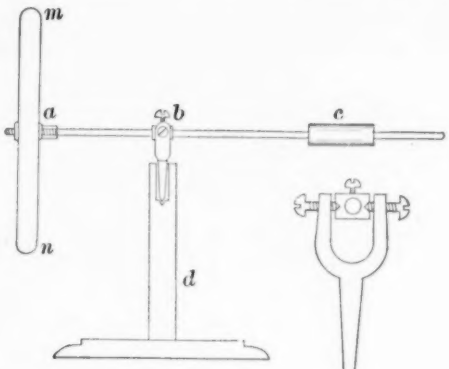


Fig. 2, Fig. 2a.

The balanced gyroscope is shown in Figs. 2 and 3. The mounting shown in Fig. 2 is formal, and brings out the points in question better than the manner of mounting shown in Fig. 3. The ⅜-inch gas pipe that is fastened directly to the axle of the wheel is not shown. The wheel *mn* is counterpoised by a weight *c* which may conveniently be a piece of lead pipe. Fig. 2a shows in detail the manner of support.

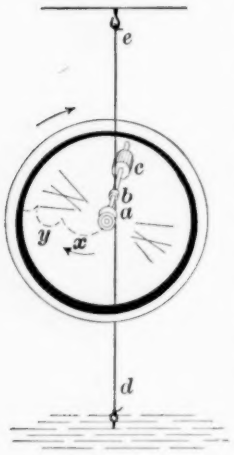


Fig. 3.

In Fig. 3 the gyroscope is simplified by supporting it from a suitable hook or a chandelier by a stout cord. To steady the apparatus the cord is continued to the floor and tightly tied to a screw-eye *d* placed directly beneath the hook *e* in the ceiling. This form of support is not as rigid as that in Fig. 2, yet the motion of the gyroscope is not appreciably affected because of this.

When the weight *c* is adjusted so that the gyroscope is balanced, there is no tendency for the axis *ac* to change its direction when the wheel is given a rotatory motion. However, if the weight *c* is moved along the axis the center of gravity of the system is changed and the gyroscope becomes a gyroscopic pendulum; if *c* is moved toward *b* it becomes a gyroscopic pendulum with its center of gravity displaced towards the fly-wheel. If the fly-wheel is given a rotatory motion, then if the weight *c* is released and the instrument left to itself precessional

motion will begin accompanied by marked oscillations. If the direction of rotation of the fly-wheel is as indicated by the arrow, *i. e.*, negative when looking along the axis from the point of support *b*, the trace of the axis of the gyroscope will be the cycloidal path *xy*, and its direction (looking down) is positive. The size and frequency of the oscillations depend upon the speed of the fly-wheel, becoming smaller and more frequent as the speed is increased. It might be well to state that the rotation is imparted to the wheel by inserting a small rod or wire nail between the spokes where they cross near the hub, and turning the wheel as by a crank of short radius. Thus a large angular velocity can be imparted to the wheel; though this is much smaller than the angular velocity of the fly-wheel of the ordinary gyroscope. Even at this comparatively small speed of rotation the gyroscope maintains the plane of its axis fairly well fixed for some time. The oscillations *xy* of the axis are noticeable until the gyroscope has precessed 6 or 7 complete revolutions. If *c* is moved away from the support we are led from geometrical considerations to expect that the precessional motion will be in the opposite direction, with the cusps of the cycloidal path pointing downward. The position of the gyroscope, cycloidal path, etc., when *c* is moved out, is given by *inverting* Fig. 3.

In Fig. 4 is represented the gyroscope in the form of a gyroscopic pendulum of considerable length. In this form, probably better than in any other, is shown the resistance offered to any change in the direction of the axis. Especially is this noticeable if the rod *af* is slightly flexible.

Fig. 4.

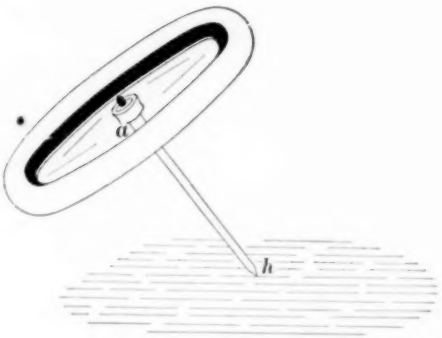


Fig. 5.

To make the apparatus assume the form of a top it is only necessary to loosen the compression nut, withdraw the rod, and insert in its place a wooden point. The top is shown in Fig. 5. If the bearings are free, the axis *ah* will not turn. It may be interesting to know that even in

this form the oscillations are noticeable, but for no longer than one revolution of precessional motion.

This form of gyroscope has several advantages over the ordinary form. The large diameter of the wheel and consequently small angular velocity make the precessional and oscillatory motions slow, thus enabling the same, especially the latter, to be followed more easily. The friction at the hub, in proportion to the masses in motion, is very much less in the bicycle wheel gyroscope because of the ball bearings. The friction at *b* (Figs. 2 and 3) is but little felt, since the lever arm *ab* is quite long. Still another advantage is its simplicity. It is within the reach of every one who possesses a bicycle. It cannot fail to attract the person who seeks merely for a qualitative explanation as well as those who wish to apply more rigid analytical methods, and it is for these reasons that the foregoing is submitted.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, June, 1900.

AN AUTOMATIC TEMPERATURE REGULATOR.

By Chas. T. Knipp.

DURING the past two years while conducting some experimental work it was necessary to maintain a piece of apparatus at constant temperatures for a day or more at a time. The range used was from room temperature to 380° C. The heating was by means of the electric current, the source of which was a 110-volt Edison dynamo. This current fluctuated under a varying load so that the heat from the coils was unsteady. Even if the current were steady some regulating device would be necessary if it were desired to keep the temperature constant for some time.

To this end an automatic regulator was devised. Two CuFe thermostats *ab*, *ab'* were clamped with their backs together as shown

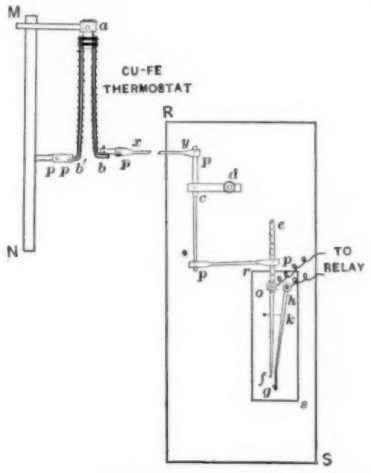


Fig. 1.

in Fig. 1. *MN*, the main support, carried at its upper end an arm *Ma* from which at *a* the thermostat was suspended by pivots. The lower end of the arm *ab'* was fastened by pivoted connections directly to the support *MN*, thus leaving the lower end of *ab* free to

move in the plane of the paper, its motion being that due to both branches of the thermostat. This motion communicated by an aluminium rod *xy* to a system of pivoted aluminium levers mounted on a vertical board *RS*. The first lever had its fulcrum on a movable support at *c* which was capable of adjustment up and down by means of a thumb-screw at *d*. The motion of the lower end of this lever was communicated to another lever *ef*. This lever was mounted on a separate board *rs*, and both lever and board were pivoted concentrically at *o* to *RS*. The lower end of *ef* terminated in a platinum ring. Another lever supported on *rs* and pivoted at *h* was held lightly against a stop *g* by a delicate spring at *k*. The lever *hg* was flattened at its lower end and carried a platinum surface on which *f* played. All of the joints *p* were delicately pivoted needle points. The amount of motion at *f* could be varied through a considerable range by adjusting the length of the levers *op* and *cp*. Wires led from *o* and *h* to a relay which in turn operated an ordinary sounder that controlled a part of the heating current.

The heating coils were in two sections ; one to heat the oven to within 5 or 10 degrees of the temperature desired, and the other to furnish the heat that was needed to keep the temperature constant by means of the regulator. By swinging *rs* about *o* the two platinum contacts could be adjusted to correspond to any temperature.

The oven consisted of a sheet iron box lined both inside and out with ¼-inch asbestos. To still further guard against radiation the oven was surrounded with an asbestos-lined wooden jacket, leaving an air-space of about two inches between the two. Windows of heavy plate glass were placed in the opposite walls of the oven and jacket. The thermostat was placed within the oven and about one inch from one of the walls. The rod *xy* extended through an opening in both walls, communicating the motion of the thermostat within to the system of levers without. Care was taken to have this opening as small as possible, yet to insure freedom of motion. The heating coils were placed at the bottom, and the bulb of the thermometer extended down to about the center of the oven. No attempt was made to screen the direct radiation from the coils. The windows enabled the coils to be seen and overheating was thus avoided.

Two curves were platted. The first (Fig. 2) shows the variation of the temperature of the oven when the apparatus was adjusted

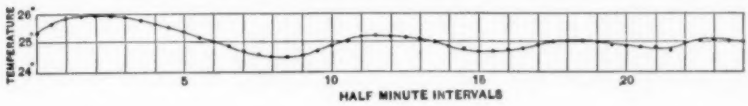


Fig. 2.

for 25, and the second (Fig. 3) when adjusted for 375 degrees centigrade. At the low temperature the first section of the heating coils was dispensed with, since the temperature was but a few degrees above that of the room. At first the variation in temperature was nearly 1½ degrees, but in the course of fifteen or twenty minutes it reached a fairly steady condition, it being some less than .5 of a degree. By better adjustment, no doubt, a less variation could have been obtained. At the high temperature both sections

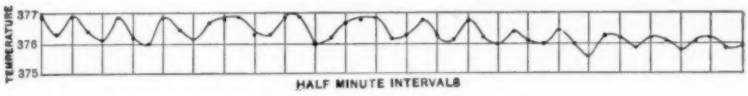


Fig. 3.

were used. The resulting curve is more broken (Fig. 3); it falls from a maximum in much less time than at the low temperature. Both curves are steeper while heating than while cooling, indicating that the regulating coil was too hot, *i. e.*, it took longer to cool through a given range of temperature than to heat through the same range. The regulation at the high temperature, after the lapse of some minutes, was within a half degree.

The essentials to success in this method of automatic temperature regulation are that the friction must be reduced to a minimum by using needle point bearings, and that the platinum contact be kept bright. An ordinary gravity cell with considerable resistance in the circuit will operate the relay.

PHYSICAL LABORATORY, CORNELL UNIVERSITY.

THE SPECIFIC INDUCTIVE CAPACITY OF DIELECTRICS IN A MAGNETIC FIELD.

BY EDWARD COLERIDGE ROBERTS.

THE experiments of Faraday and Kerr on the behavior of polarized light in passing through various media, when these are in a magnetic field, or subject to dielectric strain, make it seem possible that the presence of a magnetic field may have some effect on the specific inductive capacity of a dielectric. The following experiments were undertaken in order to discover if possible whether such an effect exists.

Although the method of attacking the problem was varied, the whole procedure was based on the fact that if a condenser be charged and insulated, any change in the specific inductive capacity will manifest itself as a change in the potential difference between the coatings.

The dielectrics studied (glass, hard rubber, and vulcanite) were used in the form of small condensers. Sheets of tinfoil 5.3 cm.^{2} were fastened on opposite sides of a plate of the dielectric, which was in each case about 20 × 25 cm., thus making the leakage path rather long. In the case of glass the whole condenser was covered with shellac to further decrease the leakage. The direction of the electric strain was parallel to the lines of magnetic force in nearly all cases.

The magnet used had 2,300 turns on each arm, and was capable of maintaining a field of 1,500 lines per cm.^{2} across an air gap of 3.5 cm., the pole pieces being 5.3 cm. square. This wide air gap was made necessary by the fact that the condenser and its connections had to be enclosed in a metallic shield, which was grounded, in order to protect them from induced charges set up by the windings of the magnet. It was found necessary to extend the shielding over the electrometer also, as otherwise the false deflections would render any accurate readings impossible.

In the first method the quadrants of the electrometer used to measure the potential of the coatings were kept charged to about 300 volts.[1] One side of the condenser was grounded and the other connected to the needle of the electrometer, and at will to one pole of a battery of 100 water cells, the other pole of which was grounded. The test as to whether proper conditions of screening had been arrived at was that no deflection should be observable when the field was established through

[1] This difference of potential was furnished by a battery of 600 water cells.

the uncharged condenser. Condenser and needle were then charged as mentioned above, and insulated. The magnetic field was then established, both directions of field being obtainable by means of a reversing switch placed in the circuit. If now a deflection of the electrometer were observed, coinciding in time with the presence of the field, it would indicate that some change had taken place in the dielectric, presumably a change in the specific inductive capacity. When such measurements were made in the case of hard rubber and vulcanite the change, if it existed, was so small as to be unobservable. A method for glass based on the rate of discharge was tried, but the results were inconclusive. The sensitiveness of the electrometer was such that a variation of potential, and therefore a change of specific inductive capacity, by an amount equal to 1/500 of the whole could have been detected.

The second method of procedure was as follows: A very constant alternating current was obtained by driving a small generator from a storage-battery-driven motor, and exciting the fields of the generator from another section of storage battery. The terminals of the generator were closed by a circuit containing one of the condensers used in the previous work, and a resistance consisting of 5 m. of lead pencil mark on ground glass. The condenser was as before held between the poles of the magnet, and it and its connections were as before enclosed in metallic shields. The potential difference across the resistance was measured by means of the electrometer, used idiostatically.

The amount of current which could flow in this circuit depended, among other things, on the specific inductive capacity of the dielectric. If, therefore, this was changed by the action of the magnetic field, the current would suffer a similar change, and this would be indicated by the variation of potential across the resistance. Inasmuch as the coatings were joined by a metallic conductor, no difficulty was experienced in getting rid of induced charges. Each of the condensers used in the previous work was studied by this method, but in no case was any change of potential evident when the magnetizing circuit was closed. The accuracy which the method permitted precluded a change in the specific inductive capacity greater than 1/200.

The third method of study, which seemed to be more accurate than either of the other two was applied to the rubber plate only. Two condensers of the same size as before were formed on the same plate, a little distance apart. The plate was so placed in the field that one was in the most intense part, and the other removed from that part by about twice the width of the air gap between the poles. The two coatings on one side were connected and grounded. Wires from the two coatings on the opposite side were connected to the opposite quadrants of the electrometer, and were so arranged that both could be charged to a

fairly high potential and insulated. The electrometer needle was charged by a spark from an electrophorous. The shielding arrangements were the same as in the other cases, and much more perfect results were obtained from the fact that the electrometer was connected to two like coatings, which were subject to the same sources of electrostatic disturbance.

If the presence of a magnetic field altered the specific inductive capacity, such a change would differ in amount in the two condensers, because the field strengths were different in the two cases, and this would have been shown by a relative change of potential between the two like coatings. This test when applied led, like the preceding ones, to negative results. Experiment showed that a potential of 1/50 volt was observable when the electrometer was used in this manner. Since the potential of the charge was about 70 volts the smallest observable change would have been 1/50 of 1/70 of the whole, or 1/3500, and this would have been the relative change of specific inductive capacity due to the field. This method therefore shows that if the suspected effect exists its value is less than 1/3500 of the whole, assuming that the magnetic field at the second condenser is small.

These experiments were merely preliminary ones, and were undertaken principally for the purpose of getting a measure of the general nature and difficulty of the problem. To get results of any real value much greater refinements of measurement, and more perfect means of eliminating disturbances, must be employed. It has seemed worth while to call attention to the work now only because the subject is one in which, so far as the writer is aware, very little work has been done.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, November, 1900.

NOTE ON THE EFFECT OF TENSION ON THE PERMANENT TORSION OF A WIRE.

By J. R. Benton.

WHEN a wire hangs free and weights are fastened to its lower end, it has been observed that a change of the weights causes the wire to twist in one direction or the other, and to come to rest at a different position. An investigation of these phenomena has been made by Himstedt.[1]

It is curious to note that similar changes in the permanent torsion of a wire are caused by increasing its tension when it is clamped fast at top and bottom, as well as when it hangs free. Such changes appear to be due to inhomogeneity and internal strains of the wire; yet great precautions to get rid of these causes failed to prevent the change in torsion from occurring. Each wire was heated twice to dull redness under the greatest safe load, and then left hanging free under a considerable load for at least twenty-four hours, before it was clamped at the bottom.

The observations were made in connection with an investigation of the dependence of the modulus of torsion on tension. Details of the arrangement and treatment of the wires will be found there.

The following table gives (in degrees of arc) the torsion of various wires, when different weights were hung on them. The wires were each about three meters long.

[1] Wiedemann's Annalen (3), Band 17, p. 701.

Weight in kgs.	3	4	5	6	7	8	10	11	14	15	18	20	23	25	30
Steel diam. 1.0 mm.							−0.9°			−0.6°		−0.5°		−0.4°	−0.4°
" " 1.5 "							−0.8°			−0.7°		−0.4°		−0.3°	−0.2°
Iron " 0.8 "	−0.1°	+0.1°		+0.2°		+0.4°	+0.5°								
" " 1.5 "							−0.4°			−0.2°		−0.1°		−0.1°	−0.1°
Copper " 0.8 "	−0.5°	0°		+0.2°		+0.3°	+0.3°								
" " 1.2 "	−1.2°		−0.8°				−0.5°			−0.1°	−0.1°				
" " 1.8 "							−0.2°			0°		0°		+0.2°	+0.3°
Nickel " 1.0 "	+0.1°		+0.4°				+0.5°			+0.5°	+0.6°				
" " 1.5 "							−0.5°			−0.4°		−0.3°		−0.2°	−0.2°
Brass " 0.8 "	−0.9°		−0.8°			−0.8°		−0.7°	−0.7°						
" " 1.5 "					0°		+0.1°			+0.1°		+0.2°	+0.2°		
Nickelin 0.8 "	0°		+0.2°				+0.2°			+0.3°	+0.3°				
" 1.5 "							−0.6°			−0.5°		−0.7°		−0.3°	−0.3°
Ger. silver 1.0 "	−0.1°		+0.3°				+0.3°			+0.5°	+0.5°				
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Bronze 0.9 "	−1.0°	−0.7°		−0.5°		−0.3°	−0.2°								

NEW BOOKS.

A Treatise on the Kinetic Theory of Gases. By S. H. BURBURY, M.A., F. R. S. Pitt Press, Cambridge. 1899.

Once more we have before us an attempt to put the kinetic theory of gases on a more secure basis. In a modest volume of 157 pages, Mr. Burbury has made an effort to examine more carefully the assumptions, tacit or otherwise, and where these are faulty or not properly carried through to their logical conclusion, to correct the formulæ. And these are not easy tasks. The problem of the subject stated briefly is as follows: To find the circumstances of the motion of a dynamical system consisting of an infinite number of separate bodies each of which may have any number of degrees of freedom. The problem is of course not even theoretically soluble without an exact specification of the forces and the initial circumstances of the motion, but by making certain assumptions we are able to arrive at some results concerning the motion of the system. It is on these assumptions that the main interest of Mr. Burbury's volume centers. Delicate questions in the theory of probability have to be negotiated and even when these are settled the mathematical pitfalls are as numerous as those encountered in finding a rigorous proof of Taylor's theorem.

The main idea of the author is best given in his own words. He says that the kinetic theory of gases "has always been treated on a certain fundamental assumption, namely, that the molecules of a gas are, as regards their relative motion, *independent* of one another. As a consequence, we may say as the expression, of that independence, the law of distribution of momenta assumes the exponential form e^{-hQ}, and, so far as concerns translation velocities,

$$Q = \Sigma m (u^2 + v^2 + w^2),$$

m being mass, and u, v, w component velocities. From this independence and from this form of Q are deduced Boltzmann's theorems, namely the H theorem, and that of the equality of mean kinetic energy, for each degree of freedom.

I propose to give to Q the more general form of a quadratic function, namely,

$$Q = \Sigma m(u^2 + v^2 + w^2) + \Sigma\Sigma b(uu' + vv' + ww').$$

Here b is a negative function of the distance r at the instant considered

between the two molecules whose velocities are u, u', etc., which function is inappreciable except for very small values of r. . . . The consequence of attributing to Q the proposed new form is, that molecules near to each other have on average a motion in the same direction. They tend to form streams."

In order, then, to clear away doubts at the outset, the author examines the conditions under which the previous form of Q has been established. There is condition A, in which the chance of any molecule having a velocity between given limits is independent of everything else but that velocity and, in particular, independent of the motions and positions of the other molecules; and condition B, in which the chance is not independent of these other circumstances. From another point of view the question is this. Can the ordinary kinetic theory, in which we search for a stationary motion, be shown to include the case where the molecules have a sensible effect on one another? If not, in what respects must the theory be altered? The condition A leads to the Maxwell distribution. To what distribution will condition B lead?

The earlier part of the book is therefore devoted to the examination of the limitations of the results obtained under condition A, and it is shown that stationary motion is impossible with the first form of Q unless the molecules are independent. After this destructive criticism the author proceeds to examine the second form of Q in the light of condition B. Stationary motion becomes possible even when the molecules do influence one another provided the coefficients v fulfill certain conditions which may be considered probable. In gases under ordinary conditions, Mr. Burbury believes that these coefficients are quite small so that no sensible error will be made by omitting them. Thus condition A, which theoretically applies only to an infinitely rare medium, is practically very little in error unless the gas becomes very dense. An interesting conclusion is that under condition B, the molecules tend to form streams and the author sees in this tendency a suggestion as to the manner in which condensation takes place under increased pressure. The argument by which he arrives at these conclusions is not, however, altogether convincing.

To follow Mr. Burbury through the various steps to the last chapter which treats of the second law of thermodynamics would lead us outside the scope of this review. For these the reader is referred to the book itself. As a mathematical treatise it will not be found to be easy reading, partly owing to the nature of the subject and partly owing to the conciseness of the author's style. An acquaintance with the earlier books of Watson, Boltzmann or Meyer will be found to be necessary for understanding his position and indeed the details of his arguments. The book thus appeals mainly to specialists and it would be ungenerous to point out its defects as a text-book. It is, in fact, the compilation of the valuable

work which Mr. Burbury has been doing for some years past and as such will be welcomed by those who take an interest in the subject and appreciate the value of Mr. Burbury's services to it.

ERNEST W. BROWN.

Introduction to Physical Chemistry. By JAMES WALKER, D.Sc., Ph.D., Professor of Chemistry in University College, Dundee.

There are few teachers of physical chemistry who have not been asked what book ought to be read before the larger text-books are undertaken? And everyone has doubtless felt the lack of any adequate work to recommend at this stage of development. It is true that the little book by Reychler on the elements of physical chemistry is both clear and concise, but it is a text-book, and a text-book as such is not what is desired at the beginning. The students of chemistry wish first to look at some length into certain interesting phases of physical chemistry, and then to take up a systematic treatment of the subject.

Professor Walker has evidently felt the need referred to and has endeavored to meet it. To quote from his preface, "This book makes no pretensions to give a complete or even systematic survey of physical chemistry. Its main object is to be explanatory. I have found in the course of ten years' experience in teaching the subject, that the average student derives little real benefit from reading the larger works which have hitherto been at his disposal, owing chiefly to his inability to effect a connection between the ordinary chemical knowledge he possesses, and the new material placed before him. He keeps his everyday chemistry and his physical chemistry strictly apart, with the result that instead of obtaining any help from the new discipline in the comprehension of his systematic or practical work, he merely finds himself cumbered with an additional burden on the memory, which is to all intents and purposes utterly useless. This state of affairs I have endeavored to remedy in the present volume by selecting certain chapters of physical chemistry, and treating the subjects contained in them at some length."

The origin of the Atomic Theory is traced and the methods of determining Atomic Weights. The development of our conception of Element, Atom and Molecule is followed up, and a table of the most accurate atomic weights is given. The Periodic System is treated both from the relation between physical properties and atomic weights, and chemical properties of the atoms and their relative weights. Chapters on Solubility, Fusion and Vaporization are followed by a clear and concise discussion of the Kinetic Theory of Gases and Van der Waal's equation.

The chapter on the Phase Rule deserves special comment. Of all the subdivisions of physical chemistry, this has hitherto impressed the student as the least satisfactory. This is not surprising when we consider in what

a mist of verbose complexity these comparatively simple matters have generally been shrouded.

Here we have for the first time in English a concise presentation of the fundamental principles which underlie this important contribution, not only to physical chemistry, but to chemistry as a whole; and it is a matter of no little pride to an American that the key to the phase law was furnished by J. Willard Gibbs.

The chapter on Osmotic Pressure and the Gas Law is followed by an Application of the Laws of Gases to Dilute Solutions, and the Freezing-point and Boiling-point methods of determining molecular weights are discussed. Under Electrolytes and Electrolysis there is taken up the method of measuring the Velocity of Ions and the Kohlrausch conductivity method. The chapters on Electrolytic Dissociation, Chemical Dynamics and Statics, Relative Strengths of Acids and Bases, and Applications of the Dissociation Theory, constitute as a whole, perhaps, the most important part of the book.

The work has been very carefully prepared, and Professor Walker has undoubtedly made a valuable contribution to physical chemical literature. The book can be heartily recommended to any student who is just beginning his career in that field which has already revolutionized chemical thought.

HARRY C. JONES.

Leçons de Chimie physique. By J. H. VAN'T HOFF; translated by M. Corvisy. Part II., Chemical Statics. Paris, A. Hermann, 1899. 16×25 cm.; 162 pp.

Under chemical statics the author discusses the "constitution of matters, atoms, molecules, structure and configuration of molecules." We have the atomic theory developed by a man who may, without much exaggeration, be called the founder of modern stereochemistry and modern physical chemistry. The subject is divided into three parts: molecular weight and polymerism; molecular structure and isomerism: molecular arrangement and polymorphism. This arrangement is not only the rational one but the historical one. It is the one we use continually in all our chemical research. When we find two different substances with the same percentage composition, we assume that there is a difference in molecular weight. If this hypothesis be disproved, we try chemical isomerism, stereochemical formulas coming in as a last resort under this head. When this fails, we throw up our hands in despair and classify our ignorance under the caption "physical isomerism."

Under the heading, molecular weight and polymerism, the main subdivisions are: molecular weight determinations in dilute gases, molecular weight determinations in dilute solutions, solid solutions. Under

molecular structure and isomerism we have a short section on the determination of constitution and a long one on the determination of configuration. The chapter on physical isomerism deals first with equilibrium relations and then with crystallographic theory. The chief characteristic of physical isomerism as the author uses the term is that it is a function of the solid state only. It is thus a property of the crystal, and for this reason the crystallographic theory finds its place in this chapter.

Apart from the clearness of arrangment and of expression, the book is to be welcomed as a step, possibly an unconscious one, in a new direction. The organic chemistry of to-day, like the inorganic chemistry of to-day, is essentially a qualitative science. We say that one substance loses water or carbonic acid, or something, when treated in a certain way, while another takes up water or hydrobromic acid, or something, when treated in some other way. Further than that we do not go. This state of things will cease so soon as we begin applying the methods and tests of physical chemistry to the problems of organic chemistry. While van't Hoff has sedulously refrained from calling attention to the fair kingdom soon to be overrun by the irrepressible vandals, the physical chemists, he has given us a most excellent map of the outlying country.

WILDER D. BANCROFT.

Scientific Papers, Vol. II. By P. G. TAIT, M.A. Cambridge, The University Press, 1900. Large 4to., cloth, pp. xiv + 500.

The scientific papers of Tait, which are now being published by The University Press, will be completed in a third volume that will contain the final papers of the author, a complete list of all his published articles and a general index. The first volume was considered in the REVIEW for August, 1899. The volume now appearing contains a number of papers on mathematical and physical subjects, among which we enumerate the following: Report on some physical properties of water, 68 pp.; on the foundations of the kinetic theory of gases, 88 pp.; on impact and the path of a rotating spherical projectile, 91 pp.; on the linear vector function, 21 pp.; the articles on thermodynamics, radiation and convection, and quaternions, from the *Encyclopædia Britannica*, 44 pp.; on the teaching of natural philosophy, 15 pp.

Altogether, the volume contains a notable collection of original papers, in which any mathematician or physicist can find much interesting and instructive matter.

We find in this volume that even the play spells of the author have yielded their contribution to science, since the articles on impact and the path of a rotating projectile, arise out of, and are constantly illustrated by, the phenomenal actions of a golf ball. For example, the fact that a

golf ball can be "jerked" nearly as far as it can be "driven," seems to have started a long train of reflections in the mind of Tait, and to have resulted in considerable laboratory, as well as field practice. Historical investigation by Tait has also revealed that Newton was familiar with the effects of rotation on a spherical projectile as exhibited by a court tennis ball, and that he gave a theoretical explanation of this effect to which no real improvement or extension had been made up to 1893, when Tait began his papers. Popular articles on the subject by Tait have appeared in *Nature*, and his popular sketch of the main results, so far as they are applicable to the game of golf, will be found in the *Badminton Magazine* for March, 1896.

The subjects of impact, rotation, resistance of the air to moving bodies, and various other phenomena pertaining to the game of golf, are still being pursued by Tait. We must naturally conclude that field practice in the game is a necessary adjunct to these pursuits, if for no other purpose than that of experimental illustration and test of scientific philosophy. The reviewer acknowledges that he has hitherto had a more partial fondness for the erratic curves and twists of a lawn tennis ball, but he has again to acknowledge his indebtedness to Tait for new light upon a subject, and to admit that a desire has been aroused to learn more of the fine points of the game of golf.

ARTHUR S. HATHAWAY.

ROSE POLYTECHNIC INSTITUTE, TERRE HAUTE, IND.

Theory of Screws. By SIR R. S. BALL. Cambridge, The University Press, 1900. 8vo, cloth, pp. xix + 544.

This publication will be welcomed by those who desire to acquire a thorough knowledge of the most recent developments in the dynamics of rigid bodies. Dr. Ball's previous volume on the subject (1876) is not only out of print, but also out of date, on account of the many important additions and extensions that have been since made by him. The present volume, contains the full development of the subject, including the latest, and from a geometrical point of view, the most important piece of work of the author. There is also a set of biographical notes on the principal works that bear upon the subject, a very complete table of contents, and an index. Appendix II. is a reprint of Dr. Ball's exceedingly pointed and humorous address to the mathematical and physical section of the British Association, in 1887, entitled, "A Dynamical Parable." The parable begins, "There was once a rigid body which lay peacefully at rest. A committee of natural philosophers was appointed to make an experimental and rational inquiry into the dynamics of that body." This parable may be regarded as a lively presentation of the trials and difficulties that beset the author in his work on the theory of screws, particularly with reference to the friendly help of the above com-

mittee of natural philosophers, Messrs Anharmonic, One-to-One, Helix, Cartesian, Commonsense, and Querulous. It is noted that Mr. Querulous objected at first to serve on the committee because the inquiry was all nonsense, and because anyhow everybody knew as much as they wished to know about the dynamics of a rigid body.

The theory of screws is founded upon the celebrated theorem of Chasles that a rigid body can be moved from one specified position to another by a rotation about a corresponding axis and a translation parallel tot hat axis, and upon the equally celebrated theorem of Poinsot that any system of forces can be replaced by a single force acting along a given axis and a couple about that axis. The motion of Chasles is called a *twist;* the force and couple of Poinsot, a *wrench.* A *screw* is an axis in a definite position with which a definite linear magnitude termed the *pitch* is associated. In a twist about a screw, the pitch is the translation along the axis per unit angle of rotation; in a wrench about a screw, the pitch is the moment of the couple per unit of the force. Thus, when a screw is specified, a twist about that screw has only its amplitude undetermined, and a wrench about it has only the intensity of the force undetermined.

The work of a twist against a wrench on specified screws, the resultants of twists and wrenches, the cylindroid, reciprocal screws, and screw coördinates, constitute the preliminary parts of the subject. The cylindroid is the locus of a screw about which the resultant of variable twists (or wrenches) on two fixed screws, will act. The surface is the locus of a line that meets an axis at right angles and moves up and down in harmonic motion, while turning uniformly round the axis in double the period of the harmonic motion. Such a line traces on a cylinder round the axis the well known curve that projects into the Lissajou curves of 1 : 2 periods. Reciprocal screws are such that a twist about one does no work against a wrench about the other. The resolution of a twist (or wrench) upon six given screws constitute the coordinates of the twist or wrench referred to the six screws. The coordinates of the screw on which the twist or wrench acts, are the same components to a unit twist or wrench. This coördinate system is a powerful one for the subject, and by taking the six screws of reference mutually reciprocal, the standard interpretations and calculations are made very simple and concise. In fact, one of the striking characteristics of the development is the simplicity and directness with which some of the most important results are obtained. It may be said, briefly, that the theory of screws presents a new set of ideas regarding the motions of a rigid body, which open up a new field for theorems that can only be stated and proven in terms of these new ideas, but which are nevertheless as important in the dynamics of a rigid body as any of the ordinary results.

There is one slip of the author that is unimportant with respect to the subject itself, but which is important as illustrating the dangers of the so-called "infinitesimal" or "indefinitely small" analysis. Ball offers, in Art. 4, p. 8, a geometrical investigation, which proves nothing-unless it be (in accordance with his assumption that the indefinitely small motions of the particles of a body are linear, that there is no indefinitely small motion except a translation. The indefinitely small motions of particles, or of rigid bodies are) in a technical sense, not to be confounded with any actual motions of the body, however small. The term "instantaneous motion" is better, and expresses a motion of the particle or body that could take place under the given conditions, and to which the actual motion of the body will more nearly approximate, the smaller the displacement of the body from its given position. In this language we put before the reader the facts of the case, stated in words that mean what they say, and not in words that must, like "indefinitely small," be considered idiomatically, since taken literally they are either meaningless or express actually an untruth. There are, of course, various "instantaneous motions" according to the character of the motion considered and the degree of approximation sought to the actual motion. In the case of a particle, we have a linear motion along the tangent line, a still better circular motion on the circle of curvature, because it takes into account the changing direction of motion, and highest of all, the motion on the osculating helix of the path. In the case of a rigid body the first approximate motion is only possible when the actual motion is a translation; the second approximate motion, only when the actual motion is a rotation. What Ball is trying to prove is then that in any rigid body moving continuously, the instantaneous motion of each particle in its osculating helix is such that the body would retain its rigidity due to such separate motions of its particles, and be twisting about a definite screw. Algebraically interpreted, the geometric investigation of Art. 4 is an attempt to prove by first differential coefficients and rigidity alone, results that depend upon the second differential coefficients as well as the first. Dr. Ball will find himself in good company in this misapplication of the deceptive infinitesimal analysis, since some of the best mathematicians from Leibnitz down have derived results both true and false by a species of infinitesimal reasoning whose logic was equally infinitesimal in value.

ARTHUR S. HATHAWAY.

ROSE POLYTECHNIC INSTITUTE.

Discourse on the Method of Rightly Conducting the Reason and Seeking Truth in the Sciences. By RENÉ DESCARTES. Translated by JOHN VEITCH. Pp. vi+87. Chicago, The Open Court Publishing Co., 1899.

Elementary Illustrations of the Differential and Integral Calculus. By AUGUSTUS DE MORGAN. Pp. viii+142. Chicago, The Open Court Publishing Co., 1899.

The Evolution of General Ideas. By TH. RIBOT. Translated by FRANCES A. WELBY. Pp. xi+231. Chicago, The Open Court Publishing Co., 1899.

The issuing of these three volumes is in accordance with the educational plan of the publishers to make more generally known the scope and methods of science.

Descartes's *Discourse on Method*, first published in Leyden in 1637, will ever be instructive, and it is particularly appropriate that this essay should be made readily accessible at this day, when so called "scientific method" is so much discussed.

De Morgan's *Calculus* is intended, aside from its interest to mathematicians, to disseminate an adequate appreciation of the methods of the calculus among the public at large. The work originally appeared in 1822, and in the present volume it is reprinted in substantially its original form.

Ribot's *Evolution of General Ideas* is a résumé of psychological lectures given in 1895.

F. B.

Electric Power Transmission, a Practical Treatise for Practical Men. (Second edition.) By LOUIS BELL. New York, Electrical World and Engineer, 1899. Pp. 505.

This new edition of a well-known work differs chiefly from the earlier edition (1897) in the addition of a chapter (XIV.) on the present state of high voltage transmission, the changes in the remainder of the book being of minor importance. As the author points out in his preface, no great advance in power transmission has been made since the issue of the earlier edition, the most important advance being transmission at high voltages and long distances, the highest voltage in commercial use advancing from 14,000 to 40,000, and the distance of transmission from 35 to 80 miles. The paper by C. F. Scott (Transactions American Institute of Electrical Engineers) on high voltage transmission, containing the result of investigations by R. D. Mershon at Telluride, Col., and by other engineers of the Westinghouse Company, is at present our most valuable source of information on this subject and forms an important part of the added chapter. The measurement of the energy losses due to brush discharge between wire and wire through the air is an important contribution to our knowledge. At 20,000 volts this charge is sufficient to be slightly luminous at night and at 50,000 volts the wires are plainly visible for a long distance.

Save for the added chapter, the book is essentially the same as the first edition; it has been the author's purpose to set forth fundamental facts and not to discuss theories of which the practical results are known.

F. BEDELL.

The Management of Dynamos. G. W. LUMMIS. Paterson.

This work is a compendium of information and advice relative to the operation of dynamos and motors. The fundamental physical conceptions of the magnetic field and the generation of an electro-motive force are given in concise form and a complete statement of the behavior of the dynamo, with its faults and their remedy, follows the introductory matter. The arrangement of numbered and lettered paragraphs, especially valuable in a reference work of this class, is to be commended, as is also the fact, that, while the book was written in England it contains nothing that does not bear directly on American practice.

HENRY H. NORRIS.

Ostwald's Klassiker der Exakten Wissenschaften, No. 110. Die Gezetze des chemischen Gleichwichtes für den verdünten gasförmigen oder gelösten Zustand. By J. H. VAN'T HOFF. Leipzig, Wilhelm Engelmann, 1900. Pp. 105.

No. 110 of Professor Ostwald's reprints contains van't Hoff's well-known paper on the laws of chemical equilibrium, translated by George Bredig. This memoir appeared originally in Swedish and since even for those who read the Scandinavian tongues the Proceedings of the Swedish Royal Academy of Science are not readily accessible, physicists and chemists alike will feel indebted to the translator and to the editor for reproducing it in this available form.

E. L. N.

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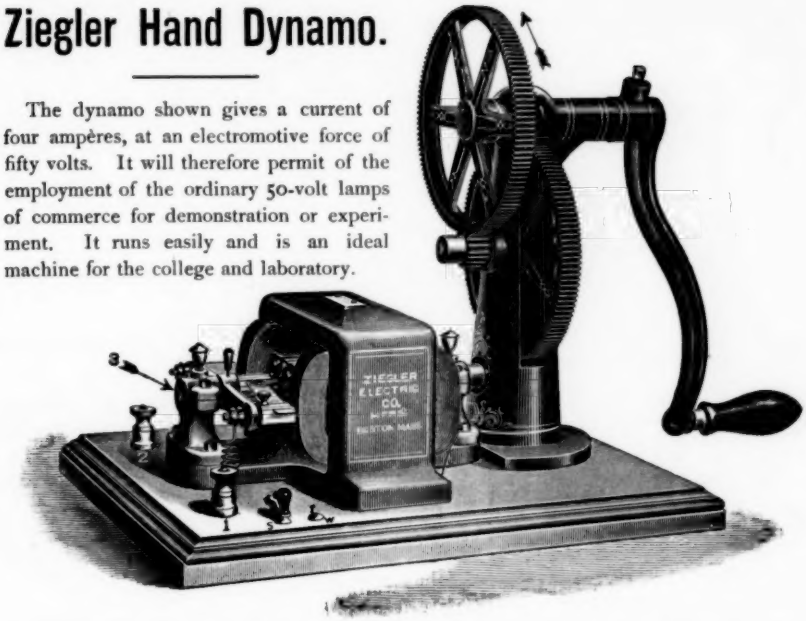

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